SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION
ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΩΝ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

LIFE Programme Contract No.: 93/GR/A14/GR/4576

Volume 3
Τόμος 3

ENVIRONMENTAL CHARACTERISATION OF LAVRION SITE - DEVELOPMENT OF REMEDIATION TECHNIQUES

ΠΕΡΙΒΑΛΛΟΝΤΙΚΟΣ ΧΑΡΑΚΤΗΡΙΣΜΟΣ ΠΕΡΙΟΧΗΣ ΛΑΥΡΙΟΥ - ΑΝΑΠΤΥΞΗ ΤΕΧΝΙΚΩΝ ΑΠΟΚΑΤΑΣΤΑΣΗΣ

National Technical University of Athens, Athens, Greece
Εθνικό Μετσόβιο Πολυτεχνείο, Αθήνα, Ελλάδα

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NATIONAL TECHNICAL UNIVERSITY OF ATHENS
DEPARTMENT OF MINING AND METALLURGICAL ENGINEERING
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GR-157 80 ZOGRAFOS, ATHENS, GREECE

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In Memoriam

Antonios Kontopoulos
Professor
(1944-1998)

Professor Antonios Kontopoulos, teacher, inspirator and Companion of the NTUA research team, passed away on April 26, 1998, a few months before the completion of this project.

Born in Chania, Crete, in 1944, he graduated from the Department of Mining and Metallurgical Engineering, National Technical University of Athens, and obtained his PhD degree in Metallurgy from McMaster University, Canada. In his professional life, he combined a close cooperation with the Mining and Metallurgical Industry with a bright academic career, which brought him international reputation and esteem. He joined the teaching staff of NTUA in 1973m and was very soon promoted to the highest academic posts.

Endued with a restless and creative mind, Professor Kontopoulos, in parallel with his teaching mission, developed an extensive research activity. He was scientific coordinator in numerous research and technology development projects, holder of patents on innovative processing techniques, and author of more than 120 original research papers in international refereed journals and conference proceedings. His work was acknowledged on an international level, and was awarded the John Philips Medal for innovative industrial research from the Mineral Industry Research Organisation of UK, and was invited as expert in several international committees for the strategic planning of research and development in the field of mining industry and environmental protection.

For the implementation of his vision, he organised in the Laboratory of Metallurgy a large and active research team to whom he transmitted his creativity and enthusiasm. We, his collaborators, shall remember him for his tireless diligence, his inspired scientific guidance, and most of all, for his radiant and kind personality.

Professor Kontopoulos had a key contribution to this project. During the last decade, he had developed an important research activity in the field of environmental management and rehabilitation of sites polluted by mining and metallurgical activities. Responding to the invitation of the Municipality of Lavreotiki, he participated actively in all the stages for the implementation of this project, from the initial overall conception of the research plan to the close supervision of the research effort for the development and application of innovative soil remediation technologies. All this work resulted in the development of an integrated environmental management scheme for the Lavrion area. He passed away unexpectedly before the completion of the project. We, the researchers involved in the project, hope that this effort has been completed successfully, and we pay tribute to his memory.

NTUA research team

Στη Μνήμη

Αντώνιου Κοντόπουλου
Καθηγητή
(1944-1998)

Λίγο πριν από την ολοκλήρωση αυτού του έργου, στις 26 Απριλίου 1998, έφυγε από κοντά μας, ο καθηγητής Αντώνης Κοντόπουλος, ο δάσκαλος, εμπνευστής και σύντροφος των προσπαθειών μας, στην ερευνητική ομάδα του Εργαστηρίου Μεταλλουργίας του ΕΜΠ.

Γεννημένος στα Χανιά το 1944, σπούδασε στη Σχολή Μηχανικών Μεταλλείων Μεταλλουργών του ΕΜΠ και εκπόνησε διδακτορική διατριβή στο Πανεπιστήμιο McMaster του Καναδά. Στην επαγγελματική του ζωή συνδύασε τη στενή συνεργασία με τη μεταλλουργική βιομηχανία, ως σύμβουλος της Fimisco και Διευθύνων Σύμβουλος της ΜΕΤΒΑ, με τη λαμπρή ακαδημαϊκή καριέρα, που του χάρισε διεθνή φήμη και αναγνώριση. Εντάχθηκε στο επιστημονικό προσωπικό του ΕΜΠ από το 1973 και πολύ σύντομα εξελίχθηκε στις ανώτερες ακαδημαϊκές βαθμίδες.

Άνθρωπος ανήσυχος κα οραματιστής, ο Αντώνης Κοντόπουλος, παράλληλα με τα διδακτικά του καθήκοντα, ανέπτυξε έντονη ερευνητική δραστηριότητα. Υπήρξε επιστημονικός υπεύθυνος πολυάριθμων ερευνητικών έργων, κάτοχος διπλωμάτων ευρεσιτεχνίας και συγγραφέας 120 πρωτότυπων επιστημονικών δημοσιεύσεων και ανακοινώσεων σε διεθνή συνέδρια και επιστημονικά περιοδικά. Το έργο του αναγνωρίσθηκε διεθνώς με πολλαπλές τιμητικές διακρίσεις. Μεταξύ άλλων, εξελέγη μέλος της Ακαδημίας Επιστημών της Νέας Υόρκης, τιμήθηκε με το βραβείο John Philips (UK) για καινοτόμο βιομηχανική έρευνα και συμμετείχε ως εμπειρογνώμονας σε πολυάριθμες διεθνείς επιτροπές για χάραξη στρατηγικής σε θέματα έρευνας και ανάπτυξης στους τομείς μεταλλευτικής βιομηχανίας και περιβαλλοντικής προστασίας.

Για την υλοποίηση του έργου του συγκρότησε στο Εργαστήριο Μεταλλουργίας πολυάριθμη και δραστήρια ερευνητική ομάδα, στην οποία μετέδωσε την πνοή και τον ενθουσιασμό του. Εμείς, οι συνεργάτες του, θα τον θυμόμαστε πάντα για την ακάματη εργατικότητά του, την εμπνευσμένη επιστημονική καθοδήγηση και κυρίως την ακτινοβολία και τη βαθιά ευγένεια της προσωπικότητάς του.

Η συμβολή του Αντώνη Κοντόπουλου στο συγκεκριμένο έργο υπήρξε καθοριστική. Την τελευταία δεκαετία είχε δώσει ιδιαίτερη βαρύτητα στον τομέα της περιβαλλοντικής διαχείρισης και αποκατάστασης περιοχών με ρύπανση από μεταλλευτικές και μεταλλουργικές δραστηριότητες. Ανταποκρινόμενος στην πρόσκληση του Δήμου Λαυρεωτικής συμμετείχε δραστήρια σε όλα τα στάδια υλοποίησης του συγκεκριμένου έργου, από την αρχική σύλληψη του ερευνητικού αντικειμένου, μέχρι τη στενή παρακολούθηση και καθοδήγηση της ερευνητικής προσπάθειας για την ανάπτυξη και εφαρμογή καινοτόμων τεχνολογιών αποκατάστασης της ρύπανσης, με τελικό στόχο τη διαμόρφωση ενός ολοκληρωμένου σχεδίου περιβαλλοντικής διαχείρισης για την περιοχή του Λαυρίου. Έφυγε από κοντά μας αιφνιδιαστικά λίγο πριν από την ολοκλήρωση του έργου. Οι ερευνητές που συνεργαστήκαμε μαζί του στο έργο, ελπίζουμε ότι ολοκληρώσαμε επάξια την προσπάθεια και αποτείνουμε φόρο τιμής στην μνήμη του.

Η ερευνητική ομάδα ΕΜΠ

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ΣΥΝΟΠΤΙΚΗ ΠΑΡΟΥΣΙΑΣΗ

ΕΙΣΑΓΩΓΗ

Η έκθεση αυτή περιλαμβάνει τις δράσεις που πραγματοποιήθηκαν από το ΕΜΠ στα πλαίσια του προγράμματος LIFE, για τον *περιβαλλοντικό χαρακτηρισμό* της περιοχής του Λαυρίου και την ανάπτυξη και εφαρμογή των κατάλληλων *τεχνικών αποκατάστασης*.

* Ο *περιβαλλοντικός χαρακτηρισμός* της περιοχής περιλαμβάνει: (1) ταυτοποίηση και χαρακτηρισμό των κύριων πηγών ρύπανσης της περιοχής και εκτίμηση των σημαντικότερων μηχανισμών απελευθέρωσης των ρύπων και (2) καθορισμό της φύσης και της έκτασης της ρύπανσης του εδάφους (βασικοί ρύποι, κινητικότητα/ βιοδιαθεσιμότητα, χωρική διασπορά και ρύπανση εις βάθος). Με βάση τα στοιχεία αυτά έγινε η επιλογή των βέλτιστων τεχνολογιών και θέσεων για την επιδεικτική εφαρμογή των μεθόδων αποκατάστασης.

* *Ανάπτυξη και εφαρμογή των κατάλληλων τεχνικών αποκατάστασης*. Με βάση τα αποτελέσματα της φάσης του περιβαλλοντικού χαρακτηρισμού, επελέγησαν τρεις κατηγορίες τεχνικών αποκατάστασης για εργαστηριακή ανάπτυξη και αξιολόγηση σε επιδεικτική κλίμακα. ερευνήθηκαν Για την αποκατάσταση των θειούχων απορριμμάτων μελετήθηκαν *τεχνικές απομόνωσης*. Τρεις εναλλακτικές μέθοδοι, που περιλαμβάνουν δύο ξηρά καλύμματα και ένα κάλυμμα με προσθήκη αλκαλικότητας, εφαρμόσθηκαν σε επιδεικτική κλίμακα στους πυρίτες Καβοδόκανου. Για την αποκατάσταση των ανθρακικών απορριμμάτων και των εδαφών διερευνήθηκε ως τεχνολογία χαμηλού κόστους η επί-τόπου *χημική σταθεροποίηση* των μετάλλων με χρήση κατάλληλων προσθέτων. Στο εργαστήριο δοκιμάσθηκαν και αξιολογήθηκαν διάφορα πρόσθετα σε διαφορετικές αναλογίες, και τα πιο επιτυχή εφαρμόσθηκαν σε επιδεικτική κλίμακα στο πεδίο. Τέλος, εξετάσθηκε η *απομάκρυνση των μετάλλων* με τη χρήση τεχνικών εκχύλισης, σαν μία εναλλακτική μέθοδος κατεργασίας που μπορεί να εξασφαλίσει την οριστική εξυγίανση των εδαφών και την μακροπρόθεσμη εξάλειψη των σχετικών περιβαλλοντικών κινδύνων.

Οι εφαρμογές επιδεικτικής κλίμακας παρείχαν πολύτιμες τεχνικές και οικονομικές πληροφορίες για την διαμόρφωση του Ολοκληρωμένου Σχεδίου Περιβαλλοντικής Διαχείρισης της περιοχής του Λαυρίου, το οποίο παρουσιάζεται σε ξεχωριστό τόμο.

ΠΕΡΙΒΑΛΛΟΝΤΙΚΟΣ ΧΑΡΑΚΤΗΡΙΣΜΟΣ ΤΗΣ ΠΕΡΙΟΧΗΣ

Οι εκτεταμένες μεταλλευτικές και μεταλλουργικές δραστηριότητες στο Λαύριο είχαν ως αποτέλεσμα τον σχηματισμό τεράστιων σωρών απορριμμάτων, που περιέχουν υψηλές συγκεντρώσεις βαρέων και τοξικών μετάλλων και συνεισέφεραν στην εκτεταμένη ρύπανση του εδάφους, καθώς και των επιφανειακών και υπόγειων υδάτων. Οι σωροί των απορριμμάτων, που αναγνωρίσθηκαν στην περιοχή παρουσιάζουν διαφορετικά γεωχημικά και περιβαλλοντικά χαρακτηριστικά και ταξινομήθηκαν σε τρεις κύριες κατηγορίες *θειούχα, ανθρακικά* και *σκουριές* (Σχήμα 1).

Τα *θειούχα* είναι απορρίμματα επίπλευσης πλούσια σε πυρίτη και βρίσκονται σε τέσσερις κύριους σωρούς γύρω από το Μεταλλουργικό εργοστάσιο του Λαυρίου και στον κόλπο του Θορικού. Η ποσότητα των θειούχων απορριμμάτων εκτιμάται ότι είναι περίπου 1.200.000 τόνοι. Τα θειούχα μεταλλεύματα που περιέχονται στους σωρούς αυτούς έχουν υποστεί φυσική οξείδωση υπό την επίδραση των υδάτων της βροχής και του ατμοσφαιρικού οξυγόνου, με αποτέλεσμα τη γένεση όξινων ρυπασμένων υδάτων. Τα νερά της επιφανειακής απορροής και τα στραγγίσματα που συσσωρεύονται στη γειτνιάζουσα περιοχή των πυριτών διαπιστώθηκε ότι είναι πολύ όξινα και περιέχουν υψηλές συγκεντρώσεις διαλελυμένων τοξικών στοιχείων, π.χ. pH 1.9, Pb 1.7ppm, Zn 1150ppm, As 800 ppm. Λόγω της μερικής οξείδωσης, τα θειούχα απορρίμματα περιέχουν ακόμη σημαντικές ποσότητες βιοδιαθέσιμων μετάλλων και χαρακτηρίζονται ως τοξικά σύμφωνα με την πρότυπη δοκιμή τοξικότητας TCLP. Οι κύριοι περιβαλλοντικοί κίνδυνοι που σχετίζονται με την παρουσία των θειούχων απορριμμάτων στην περιοχή του Λαυρίου είναι η γένεση όξινων ρυπασμένων υδάτων, τα οποία μεταφέρουν τη ρύπανση στα παρακείμενα εδάφη, και η αέρια μεταφορά των ρυπασμένων σωματιδίων, τα οποία εισπνέονται από τους ανθρώπους ή αποτίθενται στα εδάφη.

Σχήμα 1: Κύριες πήγες ρύπανσης στο Λαύριο

Τα *ανθρακικά* είναι απορρίμματα εμπλουτισμού πλούσια σε ανθρακικά ορυκτά, τα οποία έχουν αποτεθεί σε δύο κύριους σωρούς σε όλη την δυτική πλευρά της πόλης του Λαυρίου και στον κόλπο του Θορικού. Η ποσότητα τους εκτιμάται ότι ξεπερνά τους 7.000.000 τόνους. Τα απορρίμματα αυτά περιέχουν υψηλές συγκεντρώσεις ολικών και βιοδιαθέσιμων μετάλλων, π.χ. έως 35.000 ppm ολικό και 12.000 ppm βιοδιαθέσιμο Pb. Σύμφωνα με την πρότυπη δοκιμή τοξικότητας TCLP, χαρακτηρίζονται ως ιδιαίτερα τοξικά, με εκχυλίσιμο μόλυβδο έως και 230 mg/L όταν το αντίστοιχο όριο είναι 5mg/L. Καταλαμβάνουν επίσης μία εκτεταμένη περιοχή, στην οποία έχουν αναπτυχθεί σχολεία, χώροι αναψυχής και άθλησης, οικιστικές και αγροτικές δραστηριότητες. Σε καρπούς από αμπέλια και ελιές, που καλλιεργούνται πάνω σε αυτά τα απορρίμματα, μετρήθηκαν υψηλές συγκεντρώσεις μολύβδου που ξεπερνούν από 2 έως και 10 φορές τα διεθνή όρια για βρώσιμα είδη. Οι κίνδυνοι που απορρέουν από αυτούς τους σωρούς περιλαμβάνουν την άμεση επαφή των ανθρώπων με τα ρυπασμένα υλικά, την εισπνοή ή την κατάποση των αιωρούμενων σωματιδίων και την κατανάλωση λαχανικών και φρούτων, από τις συγκεκριμένες επιτόπιες καλλιέργειες.

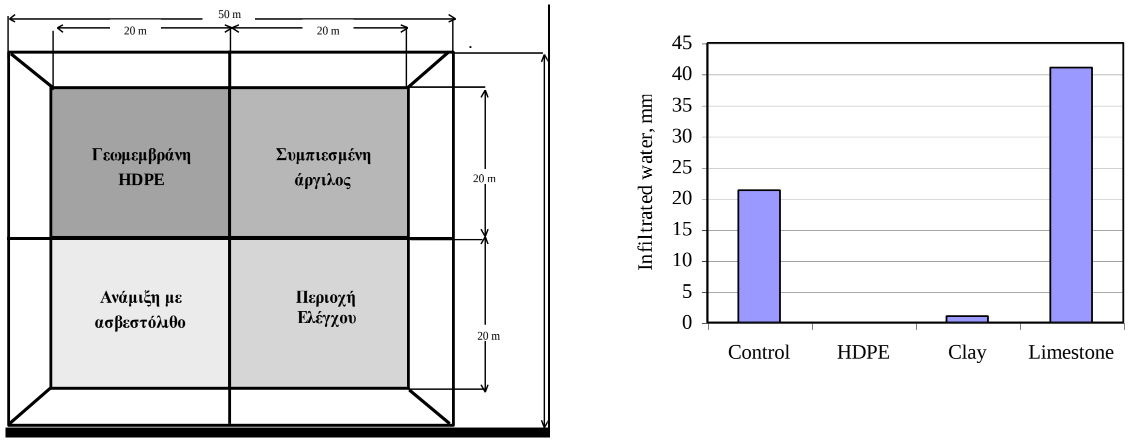
Οι *σκουριές*, που αποτελούν την τρίτη κατηγορία απορριμμάτων, είναι τα υπολείμματα της τήξης του μεταλλεύματος, με υαλώδη πυριτική σύσταση και εκτιμώμενη ποσότητα μεγαλύτερη από 5.000.000 τόνους. Στο παρελθόν οι σκουριές είχαν θεωρηθεί ως μη ενεργές και ασφαλείς για το περιβάλλον. Κατά την παρούσα μελέτη διαπιστώθηκε ότι παρατηρείται μερική διαλυτοποίηση των τοξικών μετάλλων, όταν τα μεγάλα τεμάχια της σκουριάς θραύονται σε λεπτότερα τεμαχίδια. Πάντως οι σκουριές αξιολογούνται ως λιγότερο επικίνδυνες, σε σχέση με τα υπόλοιπα απορρίμματα της περιοχής του Λαυρίου. Λόγω αδρομερούς υφής και της υαλώδους μήτρας τους, έχουν μεγάλη διαπερατότητα και περιορισμένη τάση αποσάθρωσης από τον αέρα. Οι κίνδυνοι διασποράς των ρύπων με το νερό ή τον αέρα εκτιμάται ότι είναι σχετικά μικροί.

Φυσικές διεργασίες και ανθρωπογενείς δραστηριότητες είχαν ως αποτέλεσμα την εκτεταμένη ρύπανση των εδαφών. Με βάση την ολική συγκέντρωση των ρύπων, τα μέταλλα που θα πρέπει να θεωρούνται ως πιο επικίνδυνα στα επιφανειακά εδάφη του Λαυρίου είναι το *As*, κατά δεύτερο λόγο ο *Pb* και σε μικρότερη κλίμακα το *Cd* και ο *Zn*. Όσον αφορά το αρσενικό παρατηρήθηκε ότι παρουσιάζει μικρή κινητικότητα με όλες τις εναλλακτικές δοκιμές εκχύλισης που εφαρμόσθηκαν για την εκτίμηση της κινητικότητας και διαθεσιμότητας των στοιχείων. Αντιθέτως ο μόλυβδος παρουσιάζει υψηλή εκχυλισιμότητα. Διαπιστώθηκε ότι σε έκταση μεγαλύτερη του 75% της περιοχής που εξετάσθηκε ο Pb είναι εκχυλίσιμος σε EDTA με τιμές που ξεπερνούν τα Ολλανδικά όρια (530 mg/kg), ενώ παράλληλα στο 25% αυτής της περιοχής τα εδάφη χαρακτηρίζονται ως τοξικά σύμφωνα με την πρότυπη δοκιμή TCLP. Η συσσώρευση του μολύβδου στα σταφύλια και στις ελιές παρατηρήθηκε ότι ξεπερνά τα όρια των βρώσιμων προϊόντων, ακόμη και σε εδάφη με χαμηλά επίπεδα ρύπανσης. Οι βασικοί κίνδυνοι για τον άνθρωπο είναι παρόμοιοι με αυτούς που επικρατούν στα ανθρακικά απορρίμματα και περιλαμβάνουν την άμεση επαφή, την εισπνοή και την κατάποση των ρυπασμένων σωματιδίων και την εισαγωγή των ρύπων στην τροφική αλυσίδα.

Από τη μελέτη των ειδικών χαρακτηριστικών των απορριμμάτων και των εδαφών και των περιβαλλοντικών κινδύνων που συσχετίζονται με το κάθε είδος υλικού, προέκυψαν προς διερεύνηση τρεις κατηγορίες τεχνικών αποκατάστασης. Οι τεχνικές απομόνωσης θεωρήθηκαν ότι είναι οι καταλληλότερες για τον περιορισμό των κινδύνων που σχετίζονται με τα θειούχα απορρίμματα, ενώ η χημική σταθεροποίηση και η απομάκρυνση των ρύπων εξετάσθηκαν για την αποκατάσταση των ανθρακικών απορριμμάτων και εδαφών.

ΕΛΕΓΧΟΣ ΟΞΙΝΗΣ ΑΠΟΡΡΟΗΣ – ΑΠΟΚΑΤΑΣΤΑΣΗ ΤΩΝ ΘΕΙΟΥΧΩΝ ΑΠΟΡΡΙΜΜΑΤΩΝ

Η μελέτη επικινδυνότητας των θειούχων απορριμμάτων έδειξε ότι το σχήμα αποκατάστασης θα πρέπει να εξασφαλίζει την καταστολή της όξινης απορροής και τον περιορισμό της αέριας μεταφοράς των λεπτομερών σωματιδίων των απορριμμάτων. Τρεις τεχνικές εφαρμόσθηκαν σε επιδεικτική κλίμακα στους πυρίτες Καβοδόκανου. Οι τεχνικές αυτές περιλαμβάνουν δύο ξηρά καλύμματα και ένα με προσθήκη αλκαλικότητας. Ο σωρός απορριμμάτων του Καβοδόκανου καταλαμβάνει μία έκταση 40.000 m^2, και περιέχει περίπου 600.000 t απορριμμάτων με υψηλή περιεκτικότητα σε S. Οι τρεις διαφορετικές τεχνικές αποκατάστασης εφαρμόσθηκαν σε μία έκταση 2.500 m^2, η οποία χωρίσθηκε σε 4 ισομερή τμήματα (Σχήμα 2). Το ένα τέταρτο κατασκευάσθηκε έτσι ώστε να λειτουργεί ως περιοχή ελέγχου ενώ στα υπόλοιπα τρία τμήματα εφαρμόσθηκαν οι εναλλακτικές τεχνικές αποκατάστασης. Το πρώτο ξηρό κάλυμμα κατασκευάσθηκε με τη χρήση συνθετικής γεωμεμβράνης (HDPE), η οποία λειτουργεί ως φράγμα στην διείσδυση νερού και οξυγόνου. Το δεύτερο κάλυμμα περιελάβανε τη χρήση ενός στρώματος συμπιεσμένης αργίλου. Η τρίτη λύση περιελάβανε την προσθήκη ασβεστόλιθου σε ποσοστό 20% της στοιχειομετρικά απαιτούμενης. Ο στόχος αυτής της τεχνικής ήταν να προωθήσει τις αντιδράσεις οξείδωσης - εξουδετέρωσης γύρω από τα σωματίδια του πυρίτη, ούτως ώστε να σχηματισθεί ένα αδιαπέρατο στρώμα ("hard pan") από δευτερογενή προϊόντα εξουδετέρωσης.



Σχηματικό διάγραμμα της περιοχής των δοκιμών πεδίου

Κατείσδυση υδάτων στις τέσσερις περιοχές παρέμβασης

Σχήμα 2: Εναλλακτικές τεχνικές αποκατάστασης στους πυρίτες Καβοδόκανου

Μετά από μία περίοδο παρακολούθησης δύο ετών προέκυψαν τα ακόλουθα συμπεράσματα. Η ποσότητα υδάτων, τα οποία κατεισδύουν δια μέσου των πυριτών Καβοδόκανου εάν δεν ληφθεί κανένα μέτρο αποκατάστασης (περιοχή ελέγχου), αντιστοιχεί περίπου σε $21m^3$ ανά στρέμμα ετησίως. Αυτά τα νερά είναι πολύ όξινα, pH=1.2, και περιέχουν ιδιαίτερα υψηλό φορτίο μεταλλικών ρύπων, π.χ. Fe 40 g/L, Zn 15 g/L, Mn 5.9 g/L, As 745 mg/L, και Cd 58 mg/L. Μέρος αυτής της ρύπανσης αποστραγγίζει στα γειτονικά εδάφη.

Τα δύο καλύμματα, με τη χρήση HDPE γεωμεμβράνης και στρώματος συμπιεσμένης αργίλου, έδειξαν ότι παρέχουν αποτελεσματικό φραγμό στη διείσδυση του νερού της βροχής, εμποδίζοντας έτσι την παραγωγή των όξινων υδάτων και την μετανάστευση των ρύπων. Το κάλυμμα γεωμεμβράνης λειτούργησε αποτελεσματικά ενώ δεν παρατηρήθηκε καμία αποστράγγιση νερών στην συγκεκριμένη περιοχή. Στο τμήμα όπου κατασκευάσθηκε το στρώμα της συμπιεσμένης αργίλου παρατηρήθηκε κατά την έναρξη της δεύτερης υγρής περιόδου αποστράγγιση νερών, η οποία αντιστοιχεί στο 5% περίπου του συνολικού όγκου νερών που κατεισδύουν στην περιοχή ελέγχου. Η αποστράγγιση αυτή πιθανότατα οφείλεται στην αφυδάτωση του αργιλικού στρώματος κατά την ξηρή θερινή περίοδο. Η συνεκτικότητα του αργιλικού στρώματος αποκαταστάθηκε μετά από τις πρώτες βροχοπτώσεις του Φθινοπώρου. Τέλος η προσθήκη ασβεστόλιθου είχε ως αρχικό αποτέλεσμα την αύξηση της διαπερατότητας του υλικού και του όγκου των υδάτων που κατείσδυσαν τα πρώτα δύο χρόνια.

Η εφαρμογή καλύμματος γεωμεμβράνης αποτελεί την πιο ακριβή τεχνική Το κόστος της ανέρχεται στις 4400 δρχ/ m^2 για την τοποθέτηση φύλλου γεωμεμβράνης HDPE πάχους 2mm. Με τη χρήση λεπτότερου φύλλου 1mm, το κόστος μειώνεται σε 3100 δρχ/m^2. Το κόστος του καλύμματος συμπιεσμένης αργίλου ανέρχεται στις 2800 δρχ/m^2. Ο σημαντικότερος παράγοντας που επηρεάζει την καλή συμπεριφορά του αργιλικού καλύμματος στις ξηρές κλιματικές συνθήκες του Λαυρίου είναι η αποτελεσματική προστασία της υγρασίας του, η οποία μπορεί να επιτευχθεί με τη αριστοποίηση των ανώτερων προστατευτικών στρωμάτων.

Η τεχνική της προσθήκης ασβεστόλιθου αποτελεί μία μέθοδο χαμηλού κόστους, η οποία μπορεί να λειτουργήσει αποτελεσματικά σε απορρίμματα με χαμηλή περιεκτικότητα σε S, όταν δηλαδή ο προστιθέμενος ασβεστόλιθος επαρκεί για την πλήρη εξουδετέρωση της παραγόμενης οξύτητας. Στη δοκιμή που πραγματοποιήθηκε με χρήση υποστοιχειομετρικής ποσότητας ασβεστόλιθου σε υψηλής περιεκτικότητας σιδηροπυρίτες δεν παρατηρήθηκε ο αναμενόμενος σχηματισμός του αδιαπέρατου στρώματος τουλάχιστον κατά την περίοδο παρακολούθησης των δύο ετών. Η έρευνα συνεχίζεται για τη βελτιστοποίηση της μεθόδου και την επιτάχυνση των δράσεων εξουδετέρωσης / καταβύθισης που συμβάλλουν στη δημιουργία αδιαπέρατου στρώματος.

ΜΕΘΟΔΟΙ ΧΗΜΙΚΗΣ ΣΤΑΘΕΡΟΠΟΙΗΣΗΣ

Ο σκοπός των μεθόδων σταθεροποίησης είναι ο μετασχηματισμός των ρύπων σε μορφές οι οποίες παρουσιάζουν χαμηλή διαλυτότητα και διαθεσιμότητα. Περιλαμβάνουν την επί – τόπου ανάμιξη των ρυπασμένων εδαφών με κατάλληλα υλικά και την ελεγχόμενη διαβροχή τους για κάποιο χρονικό διάστημα ώστε να πραγματοποιηθούν οι αντιδράσεις σταθεροποίησης. Ερευνήθηκαν ως μέθοδος αποκατάστασης χαμηλού κόστους για τα ανθρακικά απορρίμματα και εδάφη του Λαυρίου, τα οποία παρουσιάζουν υψηλή βιοδιαθεσιμότητα των μεταλλικών ρύπων. Οι κίνδυνοι που προέρχονται τόσο από τα ανθρακικά απορρίμματα όσο και από τα εδάφη σχετίζονται με την εισπνοή της σκόνης, καθώς και με τη βιοσυσσώρευση των βαρέων μετάλλων στα φυτά, τα οποία έτσι εισέρχονται στην τροφική αλυσίδα.

Η αποτελεσματικότητα των τεχνικών σταθεροποίησης εξετάσθηκε στα οξειδωμένα απορρίμματα «Σαβούρα». Το υλικό θεωρείται επικίνδυνο λόγω των υψηλών συγκεντρώσεων σε βαρέα μέταλλα και του υψηλού βιοδιαθέσιμου – φυτοτοξικού κλάσματος των βαρέων μετάλλων. Επίσης χαρακτηρίζεται ως τοξικό σύμφωνα με την πρότυπη δοκιμή τοξικότητας TCLP της EPA. Διάφορα ανόργανα και οργανικά απορρίμματα και χαμηλού κόστους υλικά εξετάσθηκαν ως σταθεροποιητικά μέσα. Η αποτελεσματικότητα των προσθέτων αξιολογήθηκε με τη βοήθεια χημικών και βιολογικών δοκιμών.

Τα καλύτερα αποτελέσματα παρατηρήθηκαν με τη χρήση *φωσφορικών, ιπτάμενης τέφρας και βιολογικής λάσπης*. Με την προσθήκη αυτών των υλικών, σε σχετικά μικρή ποσότητα, δηλ. περίπου 1% για τα φωσφορικά και 10% για την ιπτάμενη τέφρα και τη βιολογική λάσπη, επιτεύχθηκε η μείωση της εκχυλισιμότητας του Pb και του Cd, κάτω από τα όρια τοξικότητας. Κατά την εξέταση της φυτοδιαθεσιμότητας με εκχύλιση σε EDTA και DTPA παρατηρήθηκε μείωση της διαλυτότητας των ρύπων κατά 50 %.

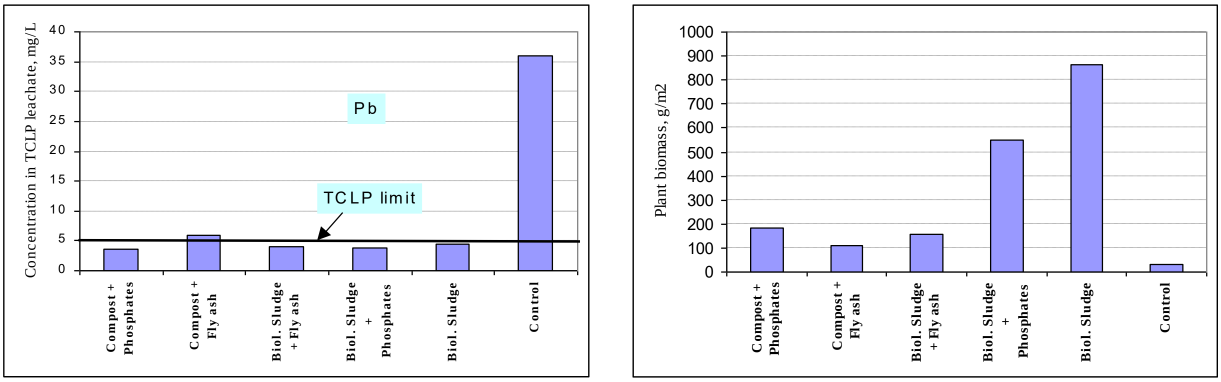
Παρά την μείωση της διαλυτότητας των βαρέων μετάλλων, η κατεργασία σταθεροποίησης δεν μπορεί να εξασφαλίσει την μείωση της φυτορρόφησης των τοξικών μετάλλων, όπως διαπιστώθηκε από την καλλιέργεια του είδους *Phaseolus Vulgaris* στα σταθεροποιημένα μίγματα. Οι συγκεντρώσεις Pb, Zn, Cd και As που συσσωρεύονται στα φύλλα παραμένουν πολύ υψηλές σε σύγκριση με τις φυσιολογικές τιμές αυτών των ιχνοστοιχείων στα φύλλα των φυτών. Οι κίνδυνοι για τον άνθρωπο μέσω της τροφικής αλυσίδας δεν εξαλείφονται με αυτή την κατεργασία και είναι σημαντικό να αποφεύγεται η καλλιέργεια βρώσιμων φυτών στο συγκεκριμένο υλικό, ακόμη και μετά την σταθεροποίησή του. Αντίθετα, η ανάπτυξη φυτικού καλύμματος με τη χρήση μη βρώσιμων φυτών μπορεί να έχει επωφελή αποτελέσματα, καθώς θα εμποδίζει την παραγωγή σκόνης και θα μειώνει τον κίνδυνο εισπνοής εν αιωρήσει ρυπασμένων σωματιδίων.

Όσον αφορά την επίδραση των προσθέτων στην ανάπτυξη των φυτών παρατηρήθηκε ότι τόσο τα φωσφορικά όσο και η ιπτάμενη τέφρα έχουν αρνητική επίδραση, ενώ τα πλούσια σε οργανική ύλη υλικά, όπως η βιολογική λάσπη και το compost, ευνοούν την παραγωγή φυτομάζας.

Συμπληρωματικά πειράματα πραγματοποιήθηκαν στο εργαστήριο χρησιμοποιώντας μίγματα από τα επιτυχημένα οργανικά και ανόργανα πρόσθετα, έτσι ώστε να συνδυασθεί η δράση τους, και να επιτευχθεί ταυτόχρονα μείωση της διαλυτότητας όλων των μετάλλων και ικανοποιητική παραγωγής φυτομάζας. Με βάση τα αποτελέσματα αυτών των πειραμάτων, επελέγησαν 5 μίγματα σταθεροποιητικών υλικών για αξιολόγηση στις δοκιμές πεδίου. Το σχήμα αποκατάστασης που εφαρμόσθηκε περιλαμβάνει την κατεργασία του εδάφους με τα μίγματα των προσθέτων για την σταθεροποίηση των βαρέων μετάλλων και την εφαρμογή φυτικού καλύμματος για την καταστολή της αέριας αποσάθρωσης.

Οι δοκιμές πεδίου, πραγματοποιήθηκαν στα απορρίμματα της Σαβούρας, θέση Νεράκι, με στόχο την αξιολόγηση της αποτελεσματικότητας αυτού του σχήματος αποκατάστασης κάτω από τις συνθήκες που επικρατούν στην περιοχή. Η περιοχή των πιλοτικών δοκιμών, περίπου 1000m^2, χωρίσθηκε σε έξι (6) ίσα τμήματα παρέμβασης. Τα σταθεροποιητικά μέσα που προστέθηκαν στις περιοχές παρέμβασης είναι: compost και φωσφορικά, ιπτάμενη τέφρα και compost, ιπτάμενη τεφρά και βιολογική λάσπη, φωσφορικά και βιολογική λάσπη, και τέλος βιολογική λάσπη. Επίσης διαμορφώθηκε μία περιοχή ελέγχου ούτως ώστε να εκτιμηθεί η αποτελεσματικότητα της σταθεροποίησης. Μετά το πέρας των εργασιών κατασκευής και διαμόρφωσης εγκαταστάθηκε στην περιοχή σύστημα τεχνητής διαβροχής και εφαρμόσθηκε ελεγχόμενη άρδευση για περίοδο ενός μήνα περίπου με στόχο την προώθηση των αντιδράσεων σταθεροποίησης. Στην περιοχή των πιλοτικών δοκιμών πραγματοποιήθηκε σπορά με μίγμα σπόρων που αποτελούνταν από διαφορά ετήσια και πολυετή φυτά.

Η προσθήκη των υλικών σταθεροποίησης μείωσε την διαλυτότητα των βαρέων μετάλλων (Pb, Zn, και Cd) σε ποσοστά που κυμαίνονται από 60 έως και 95%, και το σταθεροποιημένο υλικό χαρακτηρίζεται ως μη – τοξικό σύμφωνα με την πρότυπη δοκιμή τοξικότητας TCLP (Σχήμα 3). Διαπιστώθηκε επίσης ότι η σταθεροποίηση αποτελεί απαραίτητα στάδιο προκατεργασίας για την ανάπτυξη του φυτικού καλύμματος που δημιουργεί το επιφανειακό προστατευτικό κάλυμμα για την καταστολή της σκόνης. Στις πέντε περιοχές, στις οποίες το έδαφος αναμίχθηκε με τα υλικά σταθεροποίησης, παρατηρήθηκε πυκνή φυτοκάλυψη, η οποία αναπαράχθηκε επιτυχώς κατά τη διάρκεια της δεύτερης περιόδου ανάπτυξης. Τα φυτά, που εμφανίσθηκαν στην περιοχή ελέγχου κατά την πρώτο χρόνο, ήταν ελάχιστα και με πολύ μικρή ανάπτυξη. Η βλάστηση δεν αναπαράχθηκε και η περιοχή παρέμεινε εντελώς απογυμνωμένη κατά τη διάρκεια του δευτέρου έτους.



TCLP solubility of Pb

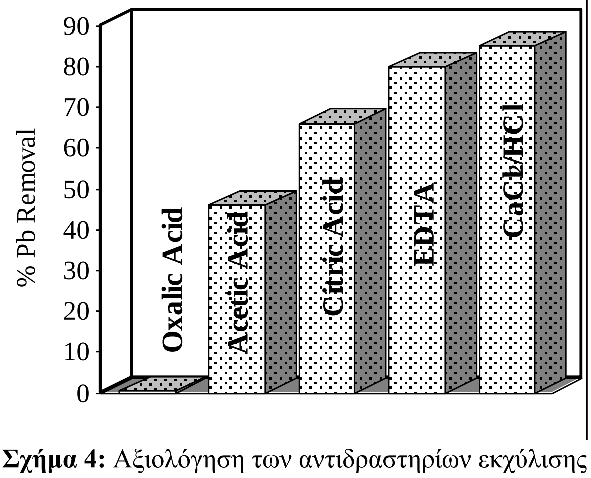
Phytomass production

Σχήμα 3: Η επίδραση της σταθεροποίησης στην διαλυτότητα Pb και στην παραγωγής φυτομάζας.

Το κόστος της αποκατάστασης όπως εφαρμόσθηκε στις πιλοτικές δοκιμές της περιοχής του Λαυρίου κυμάνθηκε από 5000 έως 9700 δρχ/m^2, με βασικότερο παράγοντα κόστους τη μεταφορά των σταθεροποιητικών υλικών στην προς αποκατάσταση περιοχή. Σημαντική θα ήταν η μείωση του κόστους με τη χρήση τοπικά παραγόμενων απορριμμάτων και υπό - προϊόντων. Για παράδειγμα με τη χρήση βιολογικής λάσπης από τη μονάδα επεξεργασίας υδατικών αποβλήτων του Λαυρίου το κόστος θα μπορούσε να μειωθεί μέχρι 1500 δρχ/m^2.

ΑΠΟΜΑΚΡΥΝΣΗ ΤΩΝ ΡΥΠΩΝ – ΤΕΧΝΙΚΕΣ ΕΚΧΥΛΙΣΗΣ

Η απομάκρυνση των ρύπων μπορεί να εξασφαλίσει μία μόνιμη λύση στα περιβαλλοντικά προβλήματα. Η κατηγορία αυτών των τεχνολογιών περιλαμβάνει όλες τις διεργασίες, οι οποίες είναι ικανές να απομακρύνουν τους ρύπους από τη μήτρα του εδάφους με φυσική ή χημική κατεργασία. Στα πλαίσια αυτού του προγράμματος διερευνήθηκε η εφαρμογή χημικών μεθόδων κατεργασίας για την απομάκρυνση των βαρέων μετάλλων από τα ανθρακικά απορρίμματα και εδάφη του Λαυρίου.



Σχήμα 4: Αξιολόγηση των αντιδραστηρίων εκχύλισης

Εξετάσθηκαν διάφορα αντιδραστήρια εκχύλισης, όπως οξαλικό οξύ, οξικό οξύ, κιτρικό οξύ, EDTA και όξινα χλωριούχα διαλύματα (Σχήμα 4). Παρατηρήθηκε ότι με τη χρήση οξαλικού οξέος δεν είναι δυνατή η απομάκρυνση των βαρέων μετάλλων. Με τη χρήση οξικού και κιτρικού οξέος επιτεύχθηκε απομάκρυνση του μολύβδου σε ποσοστά 46 και 66% αντίστοιχα από εδαφικό υλικό υψηλής ρύπανσης με αρχική περιεκτικότητα σε Pb 34000 ppm. Στο ίδιο υλικό η απομάκρυνση του μολύβδου ξεπέρασε το 80% με τη χρήση του δινάτριου άλατος EDTA και όξινου χλωριούχου διαλύματος (HCl-CaCl$_2$).

Οι τεχνικές εκχύλισης μπορούν να εφαρμοσθούν είτε με διοχέτευση του διαλύματος επί – τόπου, χωρίς εκσκαφή, είτε με κατεργασία σε σωρούς ή αντιδραστήρες μετά από εκσκαφή του εδάφους. Πειράματα σε στήλες οι οποίες προσομοιάζουν τις μεθόδους της επί – τόπου εκχύλισης και της εκχύλισης σε σωρούς πραγματοποιήθηκαν με τη χρήση των πιο επιτυχών εκχυλιστικών αντιδραστηρίων, όπως το EDTA και το διάλυμα HCl-$CaCl_2$. Τα πειράματα στις στήλες επιβεβαίωσαν ότι και τα δύο εκχυλιστικά συστήματα μπορούν να επιτύχουν πολύ υψηλά ποσοστά απομάκρυνσης των βαρέων μετάλλων (π.χ. η απομάκρυνση του Pb, του Zn και του Cd ξεπερνά το 87%). Τα καλύτερα αποτελέσματα παρατηρήθηκαν με τη χρήση του όξινου διαλύματος $CaCl_2$-HCl. Ένα ανεπιθύμητο αποτέλεσμα ήταν ότι και με τα δύο συστήματα εκχύλισης παρατηρήθηκε συνδιαλυτοποίηση σημαντικών συστατικών του εδάφους και ειδικότερα του $CaCO_3$.

Για την ανάπτυξη των ολοκληρωμένων διεργασιών εξετάσθηκαν όλα τα επιμέρους στάδια, που περιλαμβάνουν την απομάκρυνση των μετάλλων από τα κυοφορούντα διαλύματα, την αναγέννηση των αντιδραστηρίων και τον τελικό καθαρισμό του προς απόρριψη διαλύματος ώστε να ικανοποιεί τα περιβαλλοντικά όρια διάθεσης σε υδάτινους αποδέκτες. Με βάση τα πειραματικά αποτελέσματα αξιολογήθηκαν διάφορα εναλλακτικά διαγράμματα ροής με κύρια κριτήρια την ποσότητα και ποιότητα των προς απόρριψη αποβλήτων και την ελαχιστοποίηση του κόστους.

Για την απομάκρυνση των μετάλλων από εκχυλιστικά διαλύματα κιτρικού οξέος, διαπιστώθηκε ότι η χρήση *ισχυρώς όξινων κατιονικών ρητινών* αποτελεί την καλύτερη εναλλακτική τεχνική, καθώς η απομάκρυνση φθάνει περίπου το 100%. Επιπλέον το προϊόν είναι ένα αναγεννημένο όξινο διάλυμα το οποίο μπορεί να ανακυκλωθεί άμεσα στο στάδιο της εκχύλισης. Για το Na_2H_2EDTA, η καταλληλότερη τεχνική για την κατεργασία του μεταλλοφόρου διαλύματος περιλαμβάνει *δύο στάδια καταβύθισης*: αρχικά, προσθήκη NaOH για την συγκαταβύθιση του σιδήρου και του αρσενικού, και στη συνέχεια προσθήκη Na_2S για την απομάκρυνση των βαρέων μετάλλων. Στην περίπτωση του Na_2H_2EDTA εξετάσθηκε επίσης η αναγέννηση του διαλύματος μετά το στάδιο της καταβύθισης. Τα αποτελέσματα έδειξαν ότι μία ασθενώς όξινη ρητίνη μπορεί να αναγεννήσει μερικώς την αρχική οξύτητα με την προσρόφηση της περίσσειας των ιόντων του νατρίου, τα οποία εισάγονται στο διάλυμα κατά την καταβύθιση. Για την απομάκρυνση των μετάλλων από το όξινο διάλυμα του $CaCl_2$ εξετάσθηκε η καταβύθιση με $Ca(OH)_2$. Η βέλτιστη απομάκρυνση παρατηρήθηκε για pH=9, όμως οι υπολειπόμενες συγκεντρώσεις των μετάλλων δεν ικανοποιούν τους περιβαλλοντικούς κανονισμούς για διάθεση. Για τον τελικό καθαρισμό του διαλύματος εξετάσθηκε η καταβύθιση των υπολειπόμενων μεταλλικών ρύπων υπό την μορφή θειούχων.

Για να αξιολογηθεί η οικονομικότητα των μεθόδων και η ανταγωνιστικότητά τους σε σχέση με άλλες εναλλακτικές μεθόδους κατεργασίας πραγματοποιήθηκε μία αρχική ανάλυση κόστους. Για την αποκατάσταση των εδαφών με τεχνικές έκπλυσης που εφαρμόζονται βιομηχανικά από τις αρχές της δεκαετίας του '80, αναφέρεται ότι το κόστος κυμαίνεται από 50 έως 200 USD/t εδάφους, με βασικότερο παράγοντα κόστους την περιεκτικότητα του εδάφους σε λεπτομερή τεμαχίδια. Για τα κυκλώματα εκχύλισης που διερευνήθηκαν στα πλαίσια αυτού του προγράμματος, ο κύριος παράγοντας κόστους διαπιστώθηκε ότι είναι η περιεκτικότητα του εδάφους σε ασβεστίτη. Για έδαφος που περιέχει περίπου 20% $CaCO_3$, το εκτιμώμενο κόστος των αντιδραστηρίων κυμαίνεται από 22.000 έως 64.000 δρχ/t εδάφους, και ποσοστό μεγαλύτερο από 50% του κόστους αυτού οφείλεται στη διαλυτοποίηση του $CaCO_3$. Το εκτιμώμενο κόστος των αντιδραστηρίων βρίσκεται μέσα στα προαναφερθέντα όρια κόστους των βιομηχανικών μεθόδων, αλλά θα πρέπει να σημειωθεί ότι αντιπροσωπεύει μέρος μόνον του ολικού κόστους επεξεργασίας.

Οι τεχνικές εκχύλισης αποτελούν μία ακριβή κατεργασία για την εξυγίανση των εδαφών, ιδιαίτερα για ασβεστολιθικά εδάφη, όπως αυτά της περιοχής του Λαυρίου. Απαιτείται περαιτέρω έρευνα για βελτίωση της αποτελεσματικότητας και μείωση του κόστους σε επίπεδα τα οποία να καθιστούν ελκυστική την εφαρμογή αυτών των μεθόδων σε έργα αποκατάστασης μεγάλης κλίμακας.

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SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION

LIFE Project, Contract No.: 93/GR/A/4/GR/4567

VOLUME 3

ENVIRONMENTAL CHARACTERISATION OF LAVRION SITE – DEVELOPMENT OF REMEDIATION TECHNIQUES

EXECUTIVE SUMMARY

ATHENS, DECEMBER 1999

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EXECUTIVE SUMMARY

INTRODUCTION

This report summarizes the activities undertaken by NTUA in the framework of this project, for the *environmental characterisation* of Lavrion site and the development and application of appropriate *remediation techniques*.

- The *environmental characterisation* of the site includes (1) the identification and characterisation of the main pollution sources in the area and an estimation of the most important release mechanisms and (2) the determination of the nature and extent of soil contamination (key-contaminants, mobility/bioavailability, spatial distribution and in depth contamination). These data provided the basis for the selection of technologies and optimum locations for the demonstrative application of remedial methods.
- *Development and application of appropriate remediation techniques*. Based on the results of the environmental characterisation phase, three categories of techniques were selected for laboratory development and demo scale evaluation. *Isolation* techniques were investigated for the rehabilitation of sulphidic tailings. Three rehabilitation options, including two dry covers and addition of alkalinity, were evaluated on a demonstration scale on Kavodokanos pyrites. In-situ *chemical stabilisation* of metals, using appropriate additives, was investigated as a low cost treatment alternative for the remediation of carbonaceous tailings and soils. Several additives were evaluated in the laboratory and the most successful mixtures of stabilisers were tested in the field. Finally the *removal of metals*, using leaching techniques, was investigated as a treatment option which can eliminate permanently the environmental risks.

The demo scale applications provided valuable technical and financial information for the elaboration of the Integrated Environmental Management Scheme for Lavrion area, which is presented in a separate volume.

ENVIRONMENTAL CHARACTERISATION OF THE SITE

The intensive mining and metallurgical activities in Lavrion have resulted in the formation of huge spoils of wastes, containing variable amounts of heavy and toxic metals and contributing in the widespread contamination of soil, surface and ground waters. The spoils identified in the area were classified into three main categories, *sulphides, carbonates* and *slags*, exhibiting different geochemical and environmental characteristics (Figure 1).

The s*ulphides* are flotation tailings rich in pyrites. They are contained in four main stockpiles around the metallurgical plant and at Thoricos bay and their volume was estimated to approximately 1,200,000 tons. The sulphide minerals contained in the spoils are naturally oxidised under the action of meteoric water and atmospheric oxygen and this results in the generation of acidic and highly contaminated waters. Run off and seepage waters accumulated in the vicinity of pyrites were found to be very acidic and with high concentrations of dissolved toxic elements, e.g. pH 1.9, Pb 1.7ppm, Zn 1150ppm, As 800 ppm. Due to their partial oxidation, they also contain an appreciable amount of bioavailable metals and they are characterized as toxic following the TCLP test. The main environmental risks related with their presence in Lavrion area is the generation of acidic contaminated waters, which transfer the contamination to the adjacent soils, and air transfer of contaminated particles, which are inhaled by humans or deposited in the soils.

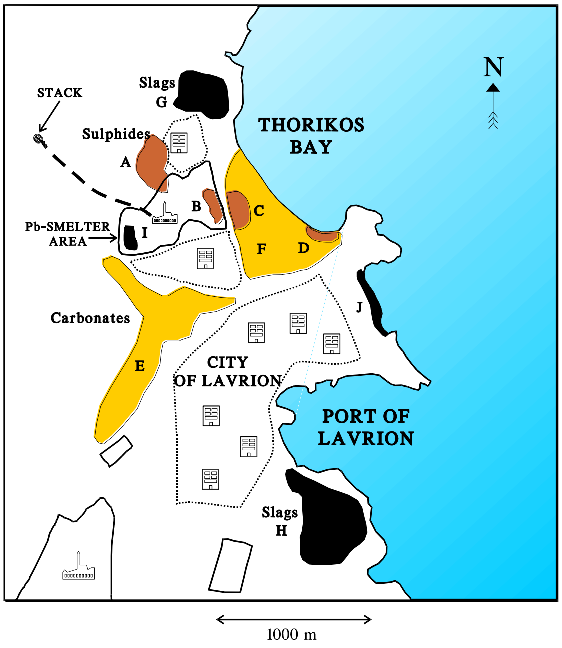


Figure 1. The main wastes in Lavrion.

The *carbonates* are beneficiation tailings rich in carbonate minerals. They are found in two main stockpiles all along the west site of Lavrion City and at Thoricos bay and their amount was estimated to more than 7,000,000 tons. They contain very high levels of total and bioavailable metals, e.g. up to 35,000ppm total and 12,000ppm bioavailable Pb. Following the TCLP test they are characterized as highly toxic, with leachable Pb up to 230 mg/L when the corresponding limit is 5mg/L. They occupy an extended area, where public, residential and agricultural activities have been developed. Grapes and olives cultivated on the top of theses tailings were found to accumulate high levels of Pb, exceeding guidelines by 2 or 10 times respectively. Risks emanating from these spoils include direct contact of humans with the contaminated material, inhalation or ingestion of airborn contaminated particles and consumption of locally grown vegetables and fruits.

The third category of wastes, *slags*, are the residue of the lead smelting operations, with a silicaceous matrix and an estimated volume of more than 5,000,000 t. Slags have been considered in the past as inactive and safe for the environment. The present study has showed that partial dissolution of toxic metals could take place, when the big slag pieces are ground to fine particles. However, slags are evaluated as less hazardous, compared to the rest tailings of Lavrion. Due to their coarse texture and their hard vitreous matrix, they have infinite water permeability and are not susceptible to wind erosion. Risks for water or air transfer of contaminants were therefore estimated as minimal.

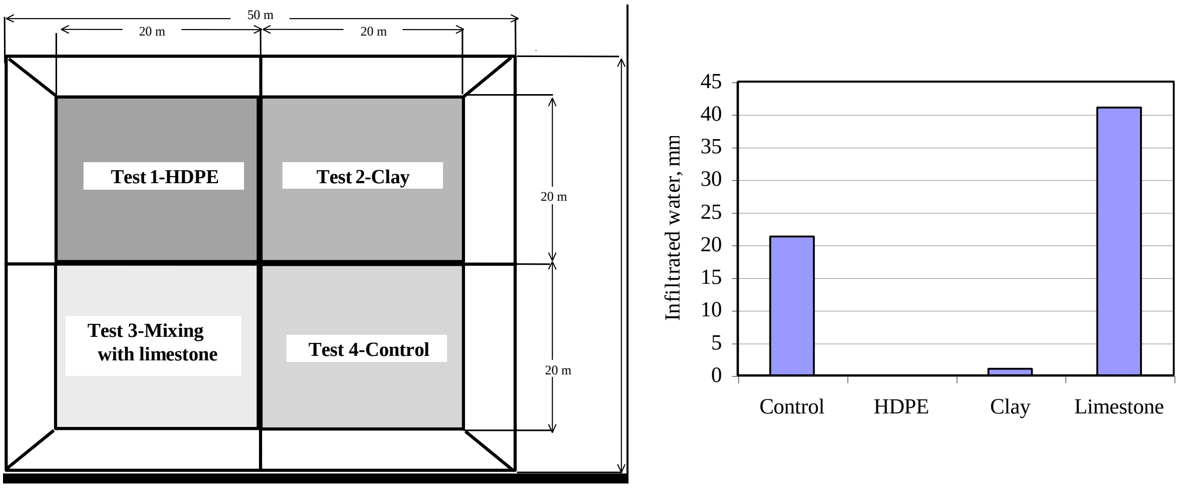
Natural processes and anthropogenic activities have resulted in the widespread contamination of soils. Based on the *total* concentration of contaminants, the primary metals of concern at Lavrion surface soils are *As* followed by *Pb* and to a lesser extent *Cd* and *Zn*. Arsenic was seen to be quite immobile with all the alternative leaching tests, which were applied to evaluate the mobility and availability of elements. On the contrary Pb was found to be highly leachable. More than 75% of the area examined contains Pb, which is leachable in EDTA at values exceeding the Netherlands intervention standards (530 mg/kg) and 25% is characterised as toxic following the TCLP procedure. Phytoaccumulation in grapes and olives was found to exceed the guidelines for edible products, even in soils with relatively low contamination. The major risks for humans are similar to that prevailing for the carbonate tailings and include the direct contact, ingestion and inhalation of contaminated particles and the introduction of contaminants to the food chain.

Considering the particular characteristics of the wastes and soils and the specific environmental risks associated with each type of material, three category of techniques were investigated: the *isolation* techniques were considered to be more suitable for eliminating the risks associated with the sulphidic tailings, while *chemical immobilisation* and *removal of metals* were evaluated for the treatment of oxidic tailings and soils.

ACID DRAINAGE CONTROL – REHABILITATION OF SULPHIDIC TAILINGS

The risk assessment study for the case of sulphidic tailings showed that the remediation scheme should aim at the reduction of acid generation potential and the elimination of wind erosion and dusting. Three rehabilitation options, including two dry covers and addition of alkalinity, were evaluated on a demonstration scale on Kavodokanos pyrites. This stockpile of pyrites covers an area of 40000 m^2 and contains approximately 600000 t of high sulphur content tailings. The three options were developed on an area of 2500 m^2, which was divided in 4 equal quadrants (Figure 2). One quadrant served as the control plot and the other three hosted the alternative remedial options. The first dry cover was constructed using a synthetic liner (HDPE) as oxygen and water barrier. The second cover involved the use of a compacted clay layer. The third solution involved the addition of limestone at an amount of 20% of the stoichiometric requirement. The objective of this technique was to promote the oxidation-neutralisation reactions around the pyrite particles in order to create an impermeable layer ("hard pan") from the secondary neutralisation products.

After a two-year monitoring period the following conclusions were drawn. The amount of water, which percolates through Kavodokanos pyrites if no action is taken (control area), corresponds to approximately 210m^3 per hectare per year. This water is very acidic, pH=1.2, and contains a very high load of metal contaminants, e.g. Fe 40 g/L, Zn 15 g/L, Mn 5.9 g/L, As 745 mg/L, and Cd 58 mg/L. Part of this contamination is released as seepage to the surrounding soils.



Plan view of the field test area — Infiltrated water in the four plots

Figure 2: Rehabilitation options tested in Kavodokanos pyrites.

The two covers, based on the use of HDPE geomembrane and a compacted clay layer respectively, were both found to provide an efficient barrier to the infiltration of rain water, suppressing thus the production of acidic waters and the migration of contaminants. The HDPE cover has effectively inhibited the percolation of water into the material and no leachate was collected from this plot. The water collected in the lysimeter of the clay cover corresponds to approximately 5% of the drainage volume produced in the control area and it is probably due to the dehydration of the clay layer during the dry summer period. The integrity of the clay layer has been re-established after the first rainfalls in autumn. Finally the addition of limestone in the fourth plot has initially increased the permeability of the material and the cumulative volume of infiltrated water corresponding to the first 2 years was increased.

The most expensive technique is the geomembrane cover, estimated to 4,400 GRD/m^2 for an HDPE sheet of 2mm. Using a thinner sheet of 1mm, the cost is reduced to 3,100 GRD/m^2. The cover incorporating compacted clay as the barrier layer had a cost of 2,800 GRD/m^2. The most crucial issue for the good performance of the clay cover under the dry climatic conditions of Lavrion is the efficient protection of its moisture, which can be achieved optimising the upper protective layers.

The limestone addition is a low cost option, which can be efficient when applied at a rate stoichiometrically equivalent to the acid generation capacity of the spoils. Substoichiometric addition of limestone to high-grade pyrites has not resulted in the expected formation of hardpan during the two years monitoring period. Research is currently in progress to optimise the technique and enhance the mechanism of hardpan formation.

CHEMICAL STABILISATION TECHNIQUES

Stabilisation methods aim at transforming the contaminants to low solubility and low availability forms. They involve mixing of the contaminated soil material in situ with appropriate substances and curing from some time in order for the reactions to proceed. They were investigated as a low-cost remedial option, for the carbonaceous tailings and soils of Lavrion, where the metal contaminants occur in highly bioavailable species. The risk assessed for both the carbonaceous tailings and soils is high and it is associated with inhalation of wind-blown dust and also with the bioaccumulation of heavy metals in the plants, which are entering in the food chain.

The efficiency of stabilisation techniques was tested on the oxidic tailings "Savoura". This material is considered as hazardous because of the elevated concentration of heavy metals and the high bioavailable-phytotoxic fraction of heavy metals. It is also characterised as toxic according to the EPA TCLP test. Several inorganic and organic wastes and low cost materials were tested as stabilising agents. The effect of these additives was evaluated with chemical and biological tests.

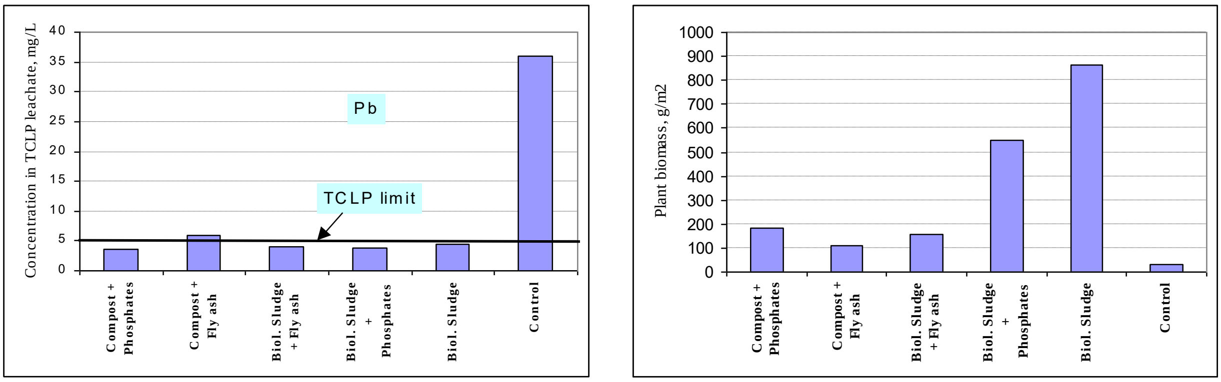
Best results were obtained using *phosphates*, *fly ash* and *biological sludge*. These additives were successful in reducing the leachability of Pb and Cd, below the regulatory TCLP limits at relatively low doses, i.e., less than 1% for phosphates and 10% for fly ash and biological sludge. The evaluation of phytoavailability by applying EDTA and DTPA tests has also indicated a 50% decrease in the solubility of contaminants.

Despite the reduction of heavy metals solubility, the stabilisation treatment was not able to reduce at safe levels the uptake of toxic elements in the plant tissues, as estimated from the cultivation of *Phaseolus Vulgaris* species on the stabilised soils. The concentrations of Pb, Zn, Cd and As accumulated in the leaves remain very high compared to the normal range encountered in the leaves of plants. Risks for humans through food intake are not eliminated with this treatment; it is thus essential to avoid the cultivation of edible plants on this soil material. On the contrary, the development of a vegetative cover using non-edible plant species could be highly beneficial, suppressing dusting and reducing the risks for the inhalation of airborn contaminated particles.

Concerning the effect of additives on the growth of plants it was found that both phosphates and fly ash had a negative effect while the organic rich materials, such as biological sludge and compost, showed a rather positive effect on the production of phytomass.

Additional laboratory experiments were conducted using mixtures of the successful inorganic and organic stabilizers in order to combine their action, reducing the solubility of all the metals and providing the appropriate substrate for phytomass production. Based on the results obtained from the above tests, five mixtures were selected for evaluation in the field. The remediation scheme, which was adopted, includes treatment of the soil with the mixtures of stabilizing agents to immobilize heavy metals and application of a vegetative cover, aiming at suppressing wind erosion.

Field tests were conducted on Savoura tailings, at location Neraki, in order to evaluate the effectiveness of this scheme under the conditions prevailing on site. The field test area, approximately 1000m^2, was divided into six (6) equal testpads. The stabilizing agents added in each testpad are: compost and phosphates, fly ash and compost, fly ash and biological sludge, phosphates and biological sludge, and finally biological sludge. Furthermore, a control test pad was constructed in order to evaluate the effectiveness of the stabilisation. A sprinkling system was installed and irrigation was applied for one month after the application of the stabilizing agents in order to promote the stabilisation reactions. The pilot area was sown with a mixture of seeds, consisting of several yearly and perennial plants.



TCLP solubility of Pb

Phytomass production

Figure 3: The effect of stabilisation on Pb solubility and phytomass production.

The addition of stabilisers has reduced the solubility of Pb, Zn, and Cd by a factor ranging between 60 and 95%, and the stabilised material was characterised as non-toxic according to the TCLP test (Figure 3). Stabilisation was also found to be an indispensable pre-treatment stage to support the development of vegetation, as a final protective cover suppressing the generation of dust. The five plots, where the soil was treated with the addition of stabilising agents, were covered with dense vegetation, which was successfully reproduced during the second growing period. Very few and poorly developed plants appeared in the control plot during the first year, but vegetation was not sustained and the area remained completely bare during the second year.

The cost of stabilisation, as applied in Lavrion field tests, was found to range between 5000 and 9700 GRD/m^2, with most important cost factor the transfer of stabilising materials to the remediation site. Considerable cost savings could be achieved using locally produced wastes and by-products. For instance, using biological sludge from Lavrion wastewater plant could reduce the costs down to 1500 GDR/m^2.

REMOVAL OF CONTAMINANTS – LEACHING TECHNIQUES

Removal of contaminants can provide a permanent solution to the environmental problem. This category of technologies includes all the processes capable of removing the pollutants from the soil matrix with the use of physical mineral processing techniques or leaching techniques. The application of leaching methods was investigated in the framework of this project for the removal of heavy metals from the carbonaceous tailings and soils of Lavrion.

Several leaching reagents were tested, such as oxalic acid, acetic acid, citric acid, EDTA and an acidic chloride solution (Figure 4). Oxalic acid was found to be inefficient for the removal of heavy metals. Acetic acid and citric acid were able to remove 46 and 66% of Pb respectively from a heavily contaminated waste material containing 3.4% Pb. Removal rates higher than 80% were obtained using the di-sodium EDTA salt and HCl-CaCl$_2$ solutions.

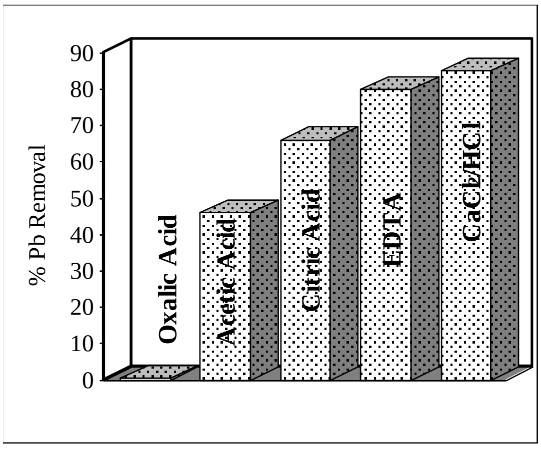


Figure 4. Evaluation of leaching reagents

Leaching techniques can be applied either in situ or by excavation and leaching on site, in heaps or using reactors. Column experiments, simulating the in situ or heap leaching techniques, were carried out using the most successful leaching reagents, i.e. the EDTA and HCl-CaCl$_2$ solutions. Column tests confirmed that both leaching systems can achieve very high removal rates for Pb, Zn and Cd exceeding 87%. Best results were obtained using the acidic brine CaCl$_2$-HCl. An undesirable side effect, observed for both leaching reagents, is the codissolution of important soil components and more particularly CaCO$_3$.

For the development of integrated processes all the subsequent treatment stages were studied, including the metals removal from the pregnant solution, the regeneration of the reagents and the final polishing of liquid effluents to meet environmental discharge regulations. *Resin treatment* and *precipitation techniques* were mainly investigated for the subsequent treatment stages. Based on the experimental results, several alternative flowsheets were evaluated, focusing to the production of environmentally compatible effluents and the minimisation of reagents costs.

The use of *strongly acidic cationic resins* seems to be a promising alternative for the removal of metals from the Citric Acid leach solutions, as it gives metal removal rates near 100%. Moreover, the product is a regenerated acid solution that can be recycled directly to the leaching stage. For the Na_2H_2EDTA process, *a two step precipitation technique* seems to be more appropriate: addition of NaOH for the coprecipitation of iron and arsenic, followed by the addition of Na_2S for the removal of heavy metals. Regeneration of the solution following the precipitation step was also tested for Na_2H_2EDTA. The results show that a weekly acidic resin can partially regenerate the initial acidity by adsorbing the excess Na^+ ions, which are introduced in the solution during precipitation. Precipitation with $Ca(OH)_2$ was tested for the removal of metals from the acidic $CaCl_2$ solution. Maximum removal was obtained at pH=9, but residual concentrations do not satisfy the environmental regulations for disposal. Precipitation of residual metal contaminants in the form of sulphides was investigated as a final polishing step. Applying this treatment, the effluent satisfies existing criteria for disposal in sewers.

A preliminary cost analysis was also carried out in order to evaluate the cost effectiveness of the processes and their competitive position towards other soil remediation alternatives. Reported treatment costs for commercial soil washing processes range between 50 and 200 USD/t soil, with most important cost factor the content of the soil in fine particles. For the leaching processes, which were investigated in this project, the crucial cost factor was found to be the calcite content of the soil. For a soil containing approximately 20% of $CaCO_3$ in its matrix, the cost of reagents was estimated to vary between 22,000 and 64,000 GRD/t soil, depending on the process, and more than 50% of this cost is due to the dissolution of $CaCO_3$. The above estimated *reagents costs* are within the cost range of existing commercial processes, but it is pointed out that they represent only part of the total treatment costs.

Leaching techniques are obviously an expensive treatment option particularly for soils rich in calcite, which are typical in the site of Lavrion. Further research is required to improve their performance and reduce the application costs to levels, which could be attractive for large-scale remediation projects.

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SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION

LIFE Project, Contract No.: 93/GR/A/4/GR/4567

VOLUME 3

ENVIRONMENTAL CHARACTERISATION OF LAVRION SITE – DEVELOPMENT OF REMEDIATION TECHNIQUES

CHAPTER 1

INTRODUCTION

ATHENS, DECEMBER 1999

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1. INTRODUCTION

1.1 Scope of the Project

The environmental pollution in the city of Lavrion originates mainly from the metallurgical activity, which is closely related with the history of the town from the antiquity until 1990, when finally stopped the production of lead.

Mining and metallurgical activities for more than 2700 years resulted in the formation of huge amounts of tailings and wastes. The disposal of these tailings has changed the initial morphology of the area. The actual city of Lavrion has been developed at the top and all around of these waste materials, containing variable amounts of toxic and heavy metals such as Pb, Zn, Cd, As, e.t.c.. Under the action of natural forces (i.e. wind and water erosion and transportation) and physicochemical actions the above materials have been subjected to physical and chemical alterations which increase the mobility and migration of toxic metals, resulting in a widespread contamination in soils and surface and underground water.

This situation has created a severe environmental problem that has seriously affected the health of the inhabitants of the Lavrion area. Epidemiological researches in the 1980's have shown that Pb content in the blood of children is well above the acceptable level set by the World Health Organization : the current WHO recommendation is that no more than 2% of the population have blood lead concentration above 20 μg/dl, while in Lavrion 50% of the population examined was found to exceed this level. As a consequence, remedial action and rehabilitation in Lavrion area is an extremely important and crucial issue for the protection of human population.

The *Municipality of Lavrion* in cooperation with the *Laboratory of Metallurgy of National Technical University of Athens (NTUA)* and the *Division of Geochemistry of the Institute of Geology and Mineral Exploration (IGME)* has undertaken to carry out the LIFE project (93/GR/A/14/GR/4576) named ***"Soil Rehabilitation in the Municipality of Lavrion"***. The objective of this project is to develop and apply, on a demonstration scale, the appropriate techniques for the rehabilitation of the heavily polluted industrial area of Lavrion.

It must be also noted that the action "Rehabilitation of contaminated soils" has been included in the **Environmental Charter** of the city and it was classified as an action of first priority for the sustainable development of the city. Larvion is the first city in Greece which has formulated its Environmental Charter, in May 1995, during its participation in the corresponding program of the DGXI of the European Union.

1.2 Project Outline

The project includes three concrete phases. Many of the actions within each phase overlap with the next in order to ensure the best possible structure of the project. A brief outline is given below:

1. Detailed Evaluation of the environmental problem

This phase includes (1) the identification and characterization of the main pollution sources in the area and an estimation of the most important release mechanisms and (2) the determination of the nature and extent of soil contamination(key-contaminants, mobility/bioavailability, spatial distribution and in depth contamination),. These data provided the basis for the selection of technologies and optimum locations for the demonstrative application of remedial methods.

2. Development and Application of the Appropriate Remediation Techniques

This phase was carried out in four steps: (1) initial screening of available technologies based on the international experience, (2) bench scale studies to identify potentially effective technologies, (3) demonstration scale application of the most appropriate techniques and (4) technical and financial assessments of the examined methods.

3. Development of an Integrated Environmental Management Scheme

The final compilation of the conclusions from the application and assessment phases has resulted in an optimal environmental model to be potentially employed for a large scale application of the methods in the Lavrion area or similar contaminated sites.

1.3 Structure of the report

This report summarises the activities undertaken by NTUA in the framework of this project, for the *environmental characterisation* of Lavrion site and the development and application of appropriate *remediation techniques*. NTUA contribution in the development of the environmental management scheme is included in the corresponding separate volume.

The *environmental characterisation* of the site is presented in Chapter 2 and includes the identification and detailed characterisation of the various categories of wastes, the characterisation of contaminated soils and the evaluation of environmental risks associated with each type of material. Based on this information, three categories of techniques were selected for laboratory development and demo scale evaluation and are presented in the following chapters.

The techniques, which were selected for the rehabilitation sulphidic tailings, aim at controlling the acid drainage generation and are presented in Chapter 3. The *chemical stabilisation* techniques, aiming at transforming the contaminants to low solubility and availability forms, were investigated as a low cost treatment option for the remediation of carbonaceous tailings and soils and are presented in Chapter 4. Chapter 5 summarises the work undertaken for the development of *leaching techniques*, aiming at the removal of heavy metals from the contaminated soil matrices. These techniques were investigated as a treatment option, which can eliminate permanently the risks.

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CHAPTER 2

EVALUATION OF THE ENVIRONMENTAL PROBLEM

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2. EVALUATION OF THE ENVIRONMENTAL PROBLEM

2.1 History of mining and metallurgy in Lavrion

Lavrion city is situated at the Southeast corner of Attica, at a distance of 75 km from Athens. The wider geographical area is called "Lavreotiki". In general, the south and east border is the Aegean coastline, the north border is a straight line directed from cape Mavrovouni to the west and the west border is a straight line directed from Legraina Bay (Cape Legraina) to the north.

The entire area of Lavreotiki is metalliferous, hilly (the highest peak of Megalo Rypari is 380 m high) and covers an area of 113 km^2 (7.5 x 15 km). During ancient times Lavreotiki was part of Athens city-state. The most important locations then were Thorikos bay, Lavrion port, Passa port and Sounion bay close to the famous Poseidon temple.

During antiquity the Athenians developed advanced mining and metallurgical techniques in order to mine the silver containing Pb ores, which were either lead oxides or lead sulphides, and produce Ag. The lead content of the ores was in general quite low and varied with the location but ores with Pb content as high as 30-50% have been reported. The Ag content depends in general upon the Pb content. It is quite probable that the ores contained an average of 2 kg of Ag per ton of contained Pb. In other words, 400 g of Ag were contained in a ton of ore with 20% Pb, so the Ag assay was approximately 0.04%. Extracting Ag from Pb was considered to be one of the most difficult metallurgical tasks (Konofagos, 1980).

The main use of Ag in those times was the production of coins, a symbol of welfare and power, and other smaller quantities were used for the production of jewellery and silverware. Apart from silver, important quantities of Pb were also produced, but Pb represented only 20% of the production cost. It is necessary to underline that ancient Greeks produced over 3,500 t of Ag and over 1,400,000 t of Pb. Approximately 70% of these quantities were produced during the 5th and 4th centuries BC.

Mining activities have been reported in Lavreotiki since the prehistoric years, but more intensively since the middle of the 6th century BC and the peak of Ag production is dated in the 5th and the 4th century B.C, during the "golden century" of the Athenian Republic. Cast lead pieces, lead oxide and other lead objects dated in 1350 B.C have been found in excavations, and archaeologists believe that lead production was known in the area some 14 centuries BC. The decline of the activities began the 3rd century, and during 1st century all activities in the area were halted. The revival of the area began with the independence of Greece the 19th century. The mining and metallurgical activities lasted for over 100 years until 1990.

The modern history of Lavreotiki

After the Greek revolution and independence in 1821, 1.5 million tn of ancient slags with an average content of 10% Pb, existed in the area and a Greek engineer, A. Kordellas, was the first one to realize the importance of these slags for the production of Ag.

In 1863 J.B. Serpieri, an Italian mining engineer, arrived at Lavrion as a representative of a French company in order to buy the rights for the treatment of the slags. The first modern metallurgical plant was built near Lavrion port by the Roux-Serpieri-Fressynet Company and Pb production began in 1865. Not only the slags but also ancient low-grade ores were treated in the plant. Because of the colonial behavior of the company, the Greek State was forced by the public opinion to take action and in 1873 the Greek national benefactor A. Syggros bought the shares from the foreign company for 11.5 million French francs. The newly established company was called "Societe des Usines" (Greek metallurgical company). In 1876 J.B. Serpieri established another company "Companie Fransaise des Mines du Laurium" in order to conduct underground survey and exploit ancient and newly found deposits. New galleries and wells were excavated and the old ones broadened. The excavation of zinc carbonate, which was discarded by the old miners within the galleries, yielded the first profits for the company. The first metallurgical factory was established at "Kyprianos" area, near Thoricos bay. The production of metallic silver containing lead began in 1878.

The Greek Company, which owned the rights for the treatment of the old slags and low-grade old ores, ceased production in 1917 after the exhaustion of these materials. In 1930 all facilities were sold and in 1944 the big chimney was brought down by the Germans. The first "Roux Serpieri" (1865-1873) company produced 60,000 t of Pb, whereas the Greek company 290,000 t between 1873-1910 and 20,000 t between 1910-1917.

The French company installed new lead treatment facilities based on the Water Jacket technique. Soft lead, lead products, sheets, red lead and lead oxides were the main products. In 1930 another French consortium, Penarroya, bought the shares from the "Roux Serpieri" company and the first differential flotation system was installed in Lavrion. The company produced 490,000 t of lead, 207,000 t between 1877-1910, 153,000 t between 1910-1939, 60,000 t between 1939-1960 and 70,000 t between 1960-1977. Mine production ceased in 1977. Between 1977-1981 Pb production was based on imported flotation concentrates originated from N. Africa. In 1981 a new company, EMMEL (National Mining and Metallurgical Company of Lavrion) was founded, buying the shares of the French company. The main shareholders were ELEVME (Greek Company of Industrial and Mining Enterprises), the community of Lavrion and the workers. All activities ceased on 19-2-90.

2-3 thousand workers were employed by the Greek Company and 3-4 thousand by the French company. It is worth noticing that modern Pb production was only 860,000 t, whereas production during ancient times was 1,400,000 t.

All this activity has created serious environmental problems in Lavrion. The work undertaken for the environmental characterisation of the site is presented in the following paragraphs.

2.2 Methodology for environmental characterisation of the site

2.2.1 Wastes

Sampling

Surface, bulk and drillcore samples were collected from all tailing dumps. Surfaces and bulk samples up to depth of 4 m were collected by the use of a mechanical excavator. Drillcore samples were collected up to depth of 15 m where possible. For the determination of some geotechnical characteristics in the laboratory, undisturbed samples were also taken. For the determination of the quality of pore water, piezometers were installed in each drillhole at a proper depth and above the water table.

Pore water monitoring

Monitoring of pore water quality was done on a bi-monthly basis for a 12-month period. The parameters measured in situ included: pH, EMF, temperature, dissolved oxygen, conductivity and total suspended solids. Elemental analysis was done by AAS in the laboratory.

Geotechnical characteristics

The main geotechnical characteristics of the wastes, such as permeability and wet bulk density were measured in situ. True density measurements were also carried out in the laboratory.

Chemical and mineralogical analysis

Elemental assays in solids were performed by digestion and measurement of the ion concentration in solution by Atomic Absorption Spectrophotometry (A.A.S.). Aqueous solutions were also analyzed with AAS. Total S was measured with a LECO Sulfur analyzer. Mineralogical analysis was carried out by optical and scanning electron microscopy and microanalysis as well as XRD techniques.

Capacity for generating acidic waters

In order to examine the potential of the spoils for acid generation, the commonly used acid base accounting technique was employed (Adam et. al., 1995). This technique is based on the assumption that the main component which generates acidity is the sulphide sulphur which is gradually oxidised to sulfuric acid, through the action of water, atmospheric oxygen and bacteria (reaction 1). The Maximum Acid Generation Potential (MAP) is thus determined by the chemical analysis of the total S content (S_t, wt%). The acidity produced can be partially neutralised by the alkaline minerals of the spoil (reaction 2). The Neutralisation Potential (NP) is determined by treating the sample with 0.1 M HCl at 90°C. The Net Neutralisation Potential (NNP) is subsequently calculated by the difference NNP= NP-MAP. Negative values of NNP indicate that the material has an overall capacity for generating acidity. All the above quantities, MAP, NP and NNP are expressed as kg of $CaCO_3$ per ton of material.

$$FeS_2 + 3.75\ O_2 + 2\ H_2O \longrightarrow Fe(OH)_3 + 2\ H_2SO_4 \qquad (1)$$

$$CaCO_3 + H_2SO_4 + 2\,H_2O \longrightarrow CaSO_4{\bullet}2H_2O + CO_2 \qquad (2)$$

Toxicity Characteristics Leaching Procedure

The US regulatory test TCLP (Toxicity Characterisation Leaching Procedure) was used to characterize the spoils in terms of toxicity. The TCLP test involves leaching of the sample with a buffer solution of acetic acid / acetic sodium 0.1M, pH=5, for 24 hours at 5% pulp density. If the dissolved metals exceed the specified limits the spoil is characterized as toxic (US EPA, 1986).

Sequential extraction

Sequential extraction tests were conducted to evaluate the actual and potential mobilisation of metals under typical environmental conditions. The scheme used in this paper is the procedure developed by Tessier *et al.* (1979). With this method the total concentration of metals is separated into five operationally defined fractions: exchangeable ($CaCl_2$), carbonate (CH_3COOH/Na), reducible ($NH_2OH.HCl$) oxidizable ($HNO_3+H_2O_2$) and residual ($HF+HClO_4$). The exchangeable and carbonate fractions represent the mobile metal species which are easily released in neutral (exchangeable) or slightly acidic (carbonate) waters and are considered as *bioavailable*. The reducible and oxidizable fractions describe the potential mobilisation under reducing or oxidizing conditions. Finally the residual fraction represents the inert forms of metals which are not expected to be released under the conditions normally encountered in nature.

Phytoavailable fraction through leaching with EDTA

This technique (Misra & Pandey 1976) has been developed by agronomists to evaluate the phytoavailable fraction of metals. 10g of sample is mixed in baker with 100ml solution CH_3COONH_4 + 0.02M EDTA and leach under stirring for 1 hour. The fraction of metals reporting to the leachate is characterized as bioavailable.

2.2.2 Contaminated soils

Contamination of surface soils

Approximately 600 samples of surface soil covering an area of 12km^2 around Lavrion were analysed using the *EDTA extraction* technique. This test, developed by agronomists for the determination of the phytoavailable fraction of toxic metals, can be considered as a "rapid screening" test. It is less expensive and time-consuming compared to the conventional analysis using acid digestion. The study was mainly focused on the four toxic metals, As, Pb, Cd and Zn, previously identified as key-contaminants in the area of Lavrion.

Selected samples, covering the whole range of contamination, were analysed for total concentrations, fractionation of metals (sequential extraction technique) and toxicity (TCLP test).

Plant sampling and analysis.

In order to evaluate directly the phytoaccumulation of toxic elements and the corresponding risks for humans, representative plant species naturally grown or cultivated were collected. The main parts of the plants, *i.e.* stems, leaves and fruits were washed, weighed, dried and analysed for the most common contaminants encountered in the area, *i.e.* Pb, Zn, Cd and As.

Depth of contamination

The depth of contamination was evaluated from drill-core samples at 23 locations (fig. 2.1). Permeability and bulk density measurements were also carried out at the same locations.

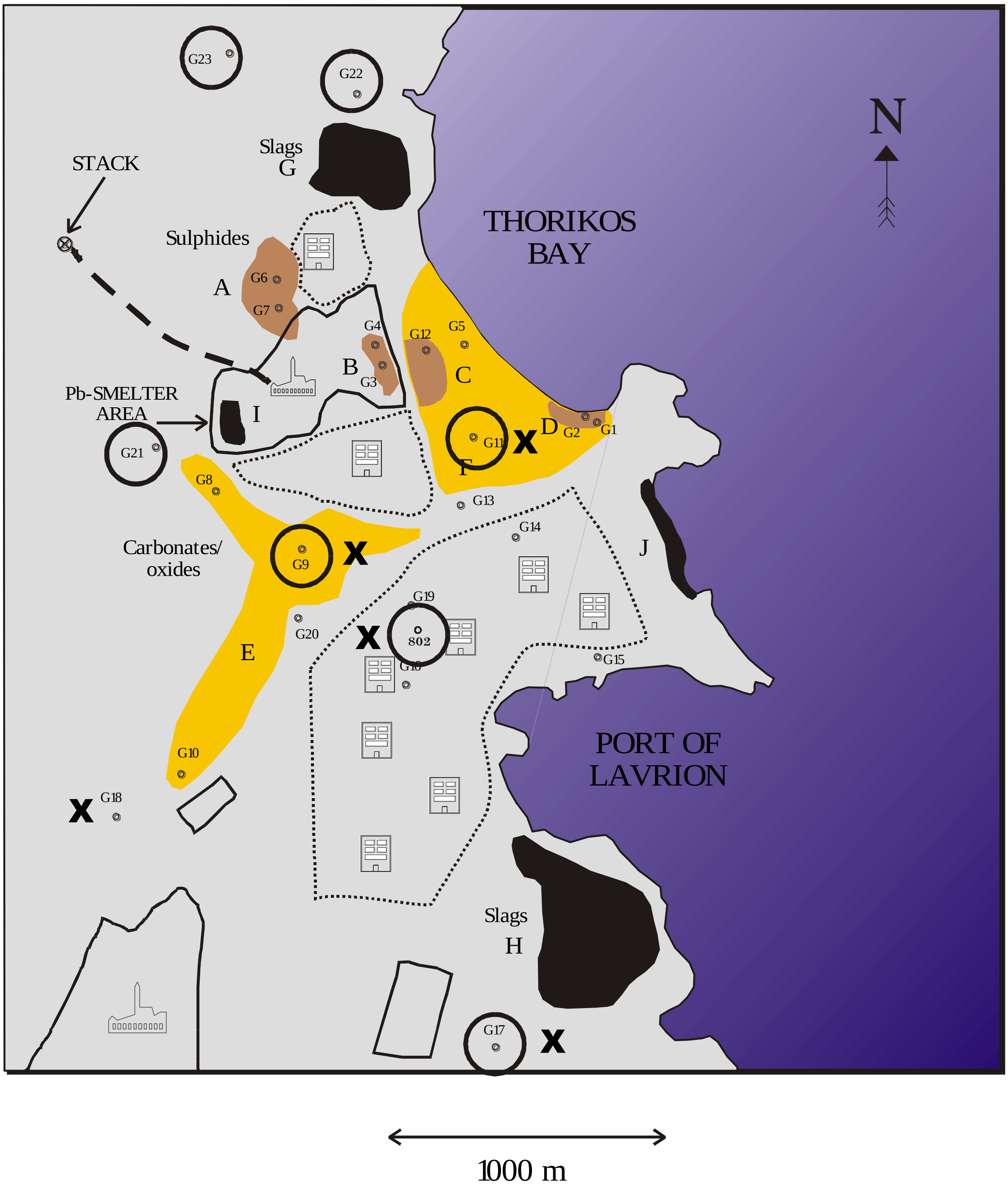


Figure 2.1. *The main wastes in Lavrion area.*

2.3 Wastes Characterisation

2.3.1 Identification of wastes

Waste materials have been deposited everywhere in the area of Lavrion City. They originate either from the milling operations, *i.e.* beneficiation tailings, or from the metallurgical operations, *i.e.* slags. The *slags* consist mainly of a silicaceous matrix, which is formed at the high temperatures prevailing during the smelting operation. The beneficiation tailings contain a wide variety of minerals, depending on the composition of the plant feed material. They are characterized as *sulphidic* or *carbonaceous* based (a) on their chemical and mineralogical composition and (b) on the overall balance between acid generating (sulphides) and alkaline minerals (mainly carbonates) evaluated with the acid base accounting technique.

The three main categories of spoils identified in Lavrion are presented in Figure 2.1 (Kontopoulos et. al., 1995). It is very difficult to estimate accurately their boundaries and real volume since a great part of the modern city has been built on them. The *sulphides* are mainly located around the old plant (A, B) and at Thoricos bay (C, D). Their volume is estimated to be 1,200,000 t. *Carbonaceous wastes* were piled all along the west side of the main residential area of Lavrion (E) or discharged and accumulated at Thoricos bay (F). Their volume is estimated to exceed 7,000,000 t. *Slags*, finally, were piled in several places around Lavrion town. Two huge stockpiles are located at the north edge of the city (G) and at Lavrion Port (H). Their amount was estimated to more than 5,000,000 t. It is pointed out that volume estimations do not include tailings and slags deposited below sea water all along the shore from Thoricos bay to Lavrion harbor.

A detailed description of the various waste stockpiles was given in several publications (Kontopoulos et al, 1995, 1996, Papassiopi et. al, 1996). The most important characteristics are summarised in tables 2.1 to 2.8 and discussed in the following paragraphs.

2.3.2 Sulphides

The sulphidic tailings are contained in four main stockpiles, with quite different characteristics. The sulphide minerals, *i.e.*, FeS_2, FeAsS, PbS, ZnS etc, represent an important percentage of their mass, varying from 5 to 60%. They contain also calcite, $CaCO_3$, and quartz, SiO_2, at variable amounts. The upper layers, which are more exhibited to the atmospheric conditions, are enriched in secondary oxidation products, *i.e.*, iron oxides, anglesite ($PbSO_4$), gypsum ($CaSO_4.H_2O$) etc. All spoils are strongly inhomogeneous vertically and horizontally.

Spoil A (Kavodokanos)

It consists of flotation tailings deposited over an area of 40,000m^2 with an average height of 10m. Total quantity is estimated at 600,000t. It is quite inhomogeneous in nature. The upper layers are rich in sulphidic minerals and poor in carbonates and have a negative NNP value of -200 kg$CaCO_3$/t, indicating the potential for acid generation. Indeed, pore water is acidic (pH=2.5) and of poor quality with very high concentrations of Zn=5000 mg/L and Cd=20 mg/L. After rainfall events, pools of acidic waters are forming at the lower levels of the spoil, with the following indicative analysis: pH=1.9, Pb=0.5, Zn=760, Cd=1,8 and As=43 mg/L. The material contains high concentrations of Pb, Zn, Cd and As up to 1%, 2.9%, 0.01% and 0.6% respectively and is characterized as toxic due to the high solubilities of Pb, Zn and Cd.

Table 2.1
Sulphides A (G6, G7): Kavodokanos Dump

PHYSICAL PROPERTIES

Quantity : 600 000 t

Dry bulk density: 1.5 g/cm^3
Permeability: 4 x 10^{-5} cm/s
Particle density: 2.7 g/cm^3
PSD: **40.21**% < 63µm

CAPACITY FOR ACID GENERATION

NNP, kg $CaCO_3$ /t	Ca, %	S, %	pH of pore water
(-**200**)-(+600)	13-15	5-10	**2.5**

TOTAL CONCENTRATION OF CONTAMINANTS, mg/kg of solid

Pb	Zn	Cd	As
2 000 - 10 000	**5 000 – 29 000**	40 - **100**	**2 000 - 6 000**

EPA-TCLP TEST, ml/l in solution

Pb	Zn	Cd	As
5-25	**645**	0.1 - **5**	< 2

** EDTA-LEACHABILITY OF CONTAMINANTS, mg/kg of solid*

Pb	Zn	Cd	As
124	**10 525**	**45**	< 20

** DISTRIBUTION OF CONTAMINANTS IN THE SEQ. EXTR. FRACTIONS, mg/kg of solid*

Fractions	Pb	Zn	Cd	As
Exchangeable	bdl	**5327**	**27.2**	
Carbonate	396	**6899**	**23.6**	
Reducible	420	5306	bdl	
Oxidisable	bdl	3405	12.5	
Residual	4120	5024	4.0	

WATER QUALITY, mg/l

pH	Pb	Zn	Cd	As	Ca	Fe	SO_4
2.5	**1.0**	**5 000**	**20**	<2	50	**300**	15 500

* Test applied in the upper drllhole sample of G7

Table 2.2
Sulphides B (G3, G4): Tailings Pond

PHYSICAL PROPERTIES

Quantity: 150 000 t

Dry bulk density: 1.26 g/cm^3
Permeability: **1.4 x 10^{-4}** cm/s
PSD: 26.8% < 63µm

CAPACITY FOR ACID GENERATION

NNP, kg $CaCO_3$ /t	Ca, %	S, %	pH of pore water
(-**200**)-(+300)	4-16	2-5	**2.3**

TOTAL CONCENTRATION OF CONTAMINANTS, mg/kg of solid

Pb	Zn	Cd	As
4 000 - 30 000	2 000 - **50 000**	10 - **200**	**1 000 - 25 000**

EPA-TCLP TEST, ml/l in solution

Pb	Zn	Cd	As
1-**18**	41.5	0.1-**4**	< 2

** EDTA-LEACHABILITY OF CONTAMINANTS, mg/kg of solid*

Pb	Zn	Cd	As
302	442	3.8	< 20

** DISTRIBUTION OF CONTAMINANTS IN THE SEQ. EXTR. FRACTIONS, mg/kg of solid*

Fractions	Pb	Zn	Cd	As
Exchangeable	140	466	6.4	
Carbonate	132	271	2.8	
Reducible	340	468	bdl	
Oxidisable	bdl	265	bdl	
Residual	3675	1709	4.0	

WATER QUALITY, mg/l

pH	Pb	Zn	Cd	As	Ca	Fe	SO_4
2.3	**2.5**	**1 300**	**6**	<2	400	**3 200**	50 000

* Test applied in the upper drillhole sample of G4

Spoil B (Tailings dam)

It consists of flotation tailings deposited into a tailing dam constructed within the metallurgical plant. It occupies 20,000 m^2 with height between 3.5-7.0 m. Total quantity is estimated at 150,000 t. The spoil is quite inhomogeneous. The surface layer exhibits negative NNP, -200 kg $CaCO_3$/t. Pore water quality in the north part is poor (pH=2.3), with high concentrations of Zn=1300 mg/L, Cd=6 mg/L and Pb=2.5 mg/L. The material contains high levels of Pb, Zn, Cd and As, up to 3%, 5%, 0.02% and 2.5% respectively and is characterized as toxic with respect to Pb and Cd.

Spoil C

Spoil C occupies a surface of 30,000m^2 with an approximate height of 8.0m. The amount is estimated at 400,000 t approximately. The average concentration of S is 8.2% but most of it, *i.e.*, 6.4%, is oxidized and precipitated in the form of gypsum, $CaSO_4.H_2O$. It exhibits a negative NNP of -120 kg $CaCO_3$/t. Pore water is slightly acidic, pH=4.8, but highly contaminated in Zn=16,000 mg/L, Cd=30 mg/L and Pb=3.2 mg/L. The material contains very high levels of Pb, Zn, Cd and As, up to 7%, 17%, 0.07% and 1.1% respectively and is characterized as toxic due to the high solubilities of Zn and Cd.

Table 2.3
Sulphides C (G12)

PHYSICAL PROPERTIES

Quantity: 400 000 t (depth 8.0 m)
Dry bulk density: 1.6 g/cm^3
Permeability: **4.2 x 10^{-4}** cm/s

CAPACITY FOR ACID GENERATION

NNP, kg $CaCO_3$ /t	Ca, %	S, %	pH of pore water
-120	6.9	8.2 (6.4% as SO4)	**4.8**

TOTAL CONCENTRATION OF CONTAMINANTS, mg/kg of solid

	Pb	Zn	Cd	As
	27 000 - 70 000	**76 000 - 171000**	**310 - 680**	**4 000 - 11 000**

EPA-TCLP TEST, ml/l in solution

	Pb	Zn	Cd	As
	4.1	**2420**	**10.6**	< 2

** EDTA-LEACHABILITY OF CONTAMINANTS, mg/kg of solid*

	Pb	Zn	Cd	As
	11 727	**41 383**	**42.8**	< 20

** DISTRIBUTION OF CONTAMINANTS IN THE SEQ. EXTR. FRACTIONS, mg/kg of solid*

Fractions	Pb	Zn	Cd	As
Exchangeable	**816**	**31396**	**145.2**	
Carbonate	**2728**	**7994**	**44.8**	
Reducible	260	4030	28.0	
Oxidisable	1775	8273	37.5	
Residual	64000	5537	8.5	

WATER QUALITY, mg/l

pH	Pb	Zn	Cd	As	Ca	Fe	SO_4
4.8	**3.2**	**16 000**	**30**	<2		**3 400**	40 000

* Test applied in the upper drillhole sample of G12

Spoil D (Bodosakis Beach pyrites)

It consists of pyritic flotation tailings deposited over an area of 14,000m^2 with an average height of 3.5 m over the beach at Thoricos bay. Total quantity is estimated at 120,000 t. The whole deposit exhibits very negative NNP up to -1000 kg$CaCO_3$/t. Acidic waters are accumulated on the tailings with the following indicative analysis: pH=1.9, Pb=0.7, Zn=1150, Cd=3.9 and As=800 mg/L. The material contains Pb, Zn, Cd and As, up to 6%, 1.2%, 0.006% and 1 % respectively and is characterized as toxic with respect to Pb, Cd and As.

Table 2.4

Sulphides D (G1, G2): Bodosakis Pyrites

PHYSICAL PROPERTIES

Quantity : 120 000 t
Dry bulk density: 1.4 g/cm^3
Permeability: 6 x 10^{-6} cm/s
PSD : **38.8** % < 63μm

CAPACITY FOR ACID GENERATION

NNP, kg $CaCO_3$ /t	Ca, %	S, %	pH of pore water
(-**1000**)-(-**200**)	1 -10	10 -32	**3-5**

TOTAL CONCENTRATION OF CONTAMINANTS, mg/kg of solid

	Pb	Zn	Cd	As
	6 000 - 60 000	1 200 - **12 000**	10 - **60**	**3 000 - 10 000**

EPA-TCLP TEST, ml/l in solution

	Pb	Zn	Cd	As
	2-**40**	17.7	0.1-**20**	0.1-**10**

** EDTA-LEACHABILITY OF CONTAMINANTS, mg/kg of solid*

	Pb	Zn	Cd	As
	2 781	386	4.5	**220**

** DISTRIBUTION OF CONTAMINANTS IN THE SEQ. EXTR. FRACTIONS, mg/kg of solid*

Fractions	Pb	Zn	Cd	As
Exchangeable	**420**	256	4.8	
Carbonate	**3016**	44	1.6	
Reducible	380	134	bdl	
Oxidisable	bdl	185	bdl	
Residual	5500	825	7.0	

WATER QUALITY, mg/l

	pH	Pb	Zn	Cd	As	Ca	Fe	SO_4
pore	**3 - 5**	**2 - 3**	**40**	**1 - 6**	<2	500	80	1 000
Surface	**1.9**	**0.7**	**1 150**	**3.9**	**800**		**10 000**	30 000

* Test applied in the upper drillhole sample of G2

2.3.3 Carbonates

The carbonaceous tailings are contained in two main spoils, known as Savoura and Telmata, in the outskirts of Lavrion town. They contain an appreciable amount of carbonate minerals, mainly calcite, representing 10 to 30% of their mass. Sulphides are detected in optical microscopy but their presence is very low, *i.e.* S<0.2%. Pb and Zn occur mainly as discrete carbonate compounds or as inclusions in Fe oxyhydroxides.

Spoil E (Savoura)

This spoil consists of gravity separation tailings, deposited over an area of 500,000 m^2 with an average height of 8m. Total quantity is estimated at 5,000,000 t. Part of the land is being used as residential. Vineyards and olive trees are grown in the area. It is a sandy and very permeable material, containing Pb, Zn, Cd and As up to 2.4%, 2.6%, 0.02% and 0.3%. This material presented a high bioavailable percentage of the heavy metals, 24% of Pb, 22% of Zn and 50% of Cd. Moreover, the material is characterized as toxic with respect to Pb and Cd. Pore water is alkaline and its quality, although poor, is far better than the one observed at the sulphidic tailings.

Spoil F (Telmata)

The spoil consists of tailings deposited over an area of 200,000m^2, with an average height of 3.8m. Total quantity is estimated at 1,200,000 t. Natural vegetation is partly covering the area. It is a fine silty-loam material, with average Pb, Zn, Cd and As concentrations about 3.7%, 2.3%, 0.01% and 0.3%. The bioavailable fraction of heavy metals is very high, 32% for Pb, 22% for Zn and 45% for Cd. Furthermore, the material is characterized as toxic with respect to Pb and Cd. Pore water is alkaline, but its quality is poor with Pb, Zn and Cd concentrations exceeding standards for drinking or irrigation purposes.

Table 2.5

Carbonates E (G8, G9, G10): Savoura

PHYSICAL PROPERTIES

Quantity: 5 000 000 t (depth =8.1m)
Dry bulk density: 1.8 g/cm^3 Permeability: **2.4 x 10^{-3}** cm/s
PSD: 17.9 % < 63μm

CAPACITY FOR ACID GENERATION

NNP, kg $CaCO_3$ /t	Ca, %	S, %	pH of pore water
	11.5 -12.7	bdl	7

TOTAL CONCENTRATION OF CONTAMINANTS, mg/kg of solid

	Pb	Zn	Cd	As
	14 700 - 24 300	**12 000 - 26 000**	**100 - 170**	**1 800 - 3 000**

EPA-TCLP TEST, ml/l in solution

	Pb	Zn	Cd	As
	87.9	207.3	**2.48**	< 2

** EDTA-LEACHABILITY OF CONTAMINANTS, mg/kg of solid*

	Pb	Zn	Cd	As
	6 152	**5 070**	**26.4**	**30**

** DISTRIBUTION OF CONTAMINANTS IN THE SEQ. EXTR. FRACTIONS, mg/kg of solid*

Fractions	Pb	Zn	Cd	As
Exchangeable	bdl	**12**	**7.2**	
Carbonate	**6612**	**6028**	**49.2**	
Reducible	14200	15290	102.0	
Oxidisable	375	615	bdl	
Residual	7000	5749	10.5	

WATER QUALITY, mg/l

pH	Pb	Zn	Cd	As	Ca	Fe	SO_4
7	< 0.5	**30**	0.1	<2		< 0.5	400

* Applied in the upper drillhole sample of G9

Table 2.6

Carbonates F (G11): Telmata

PHYSICAL PROPERTIES

Quantity: 1 200 000 t (depth =3.8m)
Dry bulk density: 1.4 g/cm^3 Permeability: **5.1 x 10^{-4}** cm/s
PSD: **75.6 %** < 63μm

CAPACITY FOR ACID GENERATION

NNP, kg $CaCO_3$ /t	Ca, %	S, %	pH of pore water
	6.6 - 8.3	bdl	7

TOTAL CONCENTRATION OF CONTAMINANTS, mg/kg of solid

	Pb	Zn	Cd	As
	37 000	**40 000**	**130**	**3 000**

EPA-TCLP TEST, ml/l in solution

	Pb	Zn	Cd	As
	232	**185**	**2.53**	< 2

** EDTA-LEACHABILITY OF CONTAMINANTS, mg/kg of solid*

	Pb	Zn	Cd	As
	15 672	40.6	**32.8**	**40**

** DISTRIBUTION OF CONTAMINANTS IN THE SEQ. EXTR. FRACTIONS, mg/kg of solid*

Fractions	Pb	Zn	Cd	As
Exchangeable	**40**	**16**	**6.4**	
Carbonate	**11848**	**6058**	**53.2**	
Reducible	11900	11066	54.0	
Oxidisable	600	1195	bdl	
Residual	10500	22068	11.5	

WATER QUALITY, mg/l

pH	Pb	Zn	Cd	As	Ca	Fe	SO_4
7	**1.7**	**8**	**2**	<2		< 0.5	5 000

* Applied in the upper drillhole sample of G11

2.3.4 Slags

Slags have been deposited in several locations in and around the city of Lavrion, on the shore and under the sea. The main stockpiles are located to the north part of the city (spoil G) and near Lavrion harbor (spoil H) and their amount is estimated 5,000,000 t. Mineralogically, they consist of a glassy silicaceous phase and several crystalline ferrosilicates. Metal contaminants are mainly found as inclusions in the above phases. Small amounts of galena (PbS) and sphalerite (ZnS) were also identified. The average concentrations of Pb, Zn, Cd and As are about 1.3%, 6.0 %, 0.02% and 0.1%.

They are found in two different forms: big irregular pieces with dimensions between 10 and 150 cm or small spherical particles of approximately 1mm. The latter were used as sandblasting material. Bioavailability and toxicity was found to be very different for the two categories of slags. The small spherical particles were found to be quite stable, with leachability below the TCLP limits. The big slag pieces, when crushed and ground, are characterized as toxic with respect to Pb. Due to their coarse texture they do not retain pore water.

Table 2.7
Slags G

PHYSICAL PROPERTIES				
Permeability: infinite				
PSD: Slag pieces greater than 10cm or pelletised slag material of 1 mm				
** TOTAL CONCENTRATION OF CONTAMINANTS, mg/kg of solid*				
	Pb	Zn	Cd	As
	10 260	**76 700**	**27**	**250**
** EPA-TCLP TEST, ml/l in solution*				
	Pb	Zn	Cd	As
	< 0.3	41.5	0.07	< 2
** EDTA-LEACHABILITY OF CONTAMINANTS, mg/kg of solid*				
	Pb	Zn	Cd	As
	161	260	0.9	< 20
** DISTRIBUTION OF CONTAMINANTS IN THE SEQ. EXTR. FRACTIONS, mg/kg of solid*				
Fractions	Pb	Zn	Cd	As
Exchangeable	bdl	**36**	5	
Carbonate	290	**4772**	8	
Reducible	1050	13240	bdl	
Oxidisable	525	15410	bdl	
Residual	8395	38500	6	

* Analyses and tests carried out on the pelletised material

Table 2.8
Slags H

PHYSICAL PROPERTIES				
Permeability: infinite				
PSD: Slag pieces greater than 10cm				
TOTAL CONCENTRATION OF CONTAMINANTS, mg/kg of solid				
	Pb	Zn	Cd	As
	10 200-18 600	**47 600-65 700**	16-20	800-1 600
EPA-TCLP TEST, ml/l in solution				
	Pb	Zn	Cd	As
	28-165	16-45	0.04-0.07	<0.5-4
EDTA-LEACHABILITY OF CONTAMINANTS, mg/kg of solid				
	Pb	Zn	Cd	As
DISTRIBUTION OF CONTAMINANTS IN THE SEQ. EXTR. FRACTIONS, mg/kg of solid				
Fractions	Pb	Zn	Cd	As
Exchangeable	**206**	**131**	/	/
Carbonate	**3121**	**4178**	5	192
Reducible	2600	10000	2	340
Oxidisable	347	7680	2	16
Residual	3675	29000	7	300

2.4 Contaminated soils

2.4.1 Key contaminants in Lavrion soils

Commencing from 1979, there have been a number of soil studies conducted in Lavrion in order to assess the contamination of soils from heavy metals (Nakos, 1979, Stavrakis and Vergou-Vichou, 1992). In the most recent sampling campaign carried out by IGME in the framework of the present LIFE project, 243 samples of surface soils from Lavrion urban area were analysed for Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Hg, Zn and Vn. The results are summarised in table 2.9 and compared to the Netherlands Intervention values for soils. It is pointed out that standards for the quality of soils exist in most European and North American countries, but they are based on different approaches. For instance, the Netherlands have established two levels of screening values, indicating the required actions, *i.e.*, *target values* as background levels, and *intervention values* suggesting remedial measures. On the contrary, Canadian standards are based on the use of land, *i.e.*, agricultural, residential/parkland, commercial and industrial (see Appendix A1). The Dutch Intervention values have been used in this study for a preliminary identification of the key contaminants. It is worthwhile to notice that the Dutch Intervention values were derived from a combination at human-toxicological and ecotoxicological studies (Van den Berg, et. al., 1993). In most cases, the ecosystem was found to be much sensitive to the presence of heavy metals compared to humans. Intervention values, based only on human–toxicological data, are presented in parenthesis in table 2.9 and are in most cases several orders of magnitude higher compared to the integrated intervention values, which incorporated the protection of the ecosystem. Particularly for Pb ecotoxicological and human toxicological studies have led to similar limits, *i.e.*, 290 and 300 mg/kg respectively, but a higher intervention value, *i.e.* 530 mg/kg, was finally adopted.

Table 2.9
Contamination of surface soils in Lavrion (IGME, 1999)
compared to Netherlands Intervention Values (n=243)

	Lavrion Soil Samples, mg/kg			**Dutch Intervention Values**		**Ratio Median/ Intervention values**	
	Min	**Max**	**Median**	**Integrated***	**Human Toxicological**	**Integrated**	**Human Toxicological**
Sb	28	567	151	-	-	-	
As	50	24000	1290	55	(680)	**23.5**	**(1.9)**
Ba	64	4555	479	625	(4300)	0.77	(0.11)
Be	0.2	2.7	1	-	-	-	-
Cd	4	925	38	12	(35)	**3.2**	**(1.09)**
Cr	2	1083	183	380	(2250)	0.6	(0.08)
Cu	43	4445	186	190	(16000)	0.98	(0.01)
Pb	810	151579	7305	530	(300[1])	**13.8**	**(24.4)**
Hg	0.001	0.728	0.117	10	(200)	0.01	(<0.01)
Ni	40	591	127	210	(6600)	0.6	(0.02)
Va	26	325	75	-	-	-	-
Zn	591	76310	6668	720	(56000)	**9.3**	(0.12)

*They incorporate ecotoxicological and human toxicological studies. In parenthesis intervention values based only on human toxicological data

[1] For children

Based on the *Integrated Intervention Values*, the primary metals of concern are **As**, followed by **Pb** and to a lesser extent **Zn** and **Cd**. The human toxicological intervention values of Netherlands indicate Pb as primary contaminant, followed by As and Cd. It is pointed out that for some elements estimations about their effect on human health are still uncertain and this may lead to very different soil standards amongst the countries. For instance, US EPA (1998) has classified As to the carcinogenic elements and the suggested Preliminary Remediation Goals for the protection of human health are very low, *i.e.* 0.3 mg/kg for residential areas and 3 mg/kg for industrial areas.

2.4.2 EDTA - leachable fraction of contaminants

The particularity of metal contaminants in soils is that only part of them is soluble and available to the biotic environment. Most international soil standards are based on toxicological studies, where metal contaminants are fed to animals in the form of *soluble* salts. This may lead to an overestimation of the risks when *total* concentrations in soils are compared against standards, which are derived using soluble metal species. This is a problem widely recognized, but unfortunately there is not yet a standard and widely accepted leaching procedure to distinguish between total and available concentration of metals.

The EDTA leaching test has been used in this study to estimate the leachable fraction of contaminants in Lavrion surface soils. This test, developed by agronomists for the determination of the phytoavailable fraction of toxic metals, can be considered as a "rapid screening" test. Approximately 600 samples of surface soil covering an area of 12 km^2 around Lavrion were analysed using the EDTA leaching technique. The results are summarised in table 2.10, in comparison with the Dutch Intervention values for soils.

Table 2.10: Soluble fraction of contaminants in Lavrion soils, using the EDTA leaching test (n=616)

	EDTA leachable metals, mg/kg			Dutch Intervention values	Ratio Median/ Intervention values
	Min	Max	Median		
As	<20	950	20	55	0.36
Cd	0.4	120	7.5	12	0.62
Pb	12	15100	1200	530	**2.26**
Zn	8	9900	239	720	0.33

The EDTA leachable fraction of As, Cd, Pb and Zn was found to exceed Dutch Intervention values for 21%, 34%, 76% and 19% respectively. The median value (50%) exceeded standards only for Pb.

Spatial distribution

In order to evaluate the spatial distribution of leachable contaminants, the 616 samples were grouped into 156 grid squares of 250 meters. The soil sample analyses were averaged per square and the results were transferred to the map. Figure 2.2 shows the distribution of contamination for Pb. The most heavily polluted areas extend to the south of Pb-smelter, around the stockpile E of washing tailings. A similar pattern is observed for all the four contaminants examined.

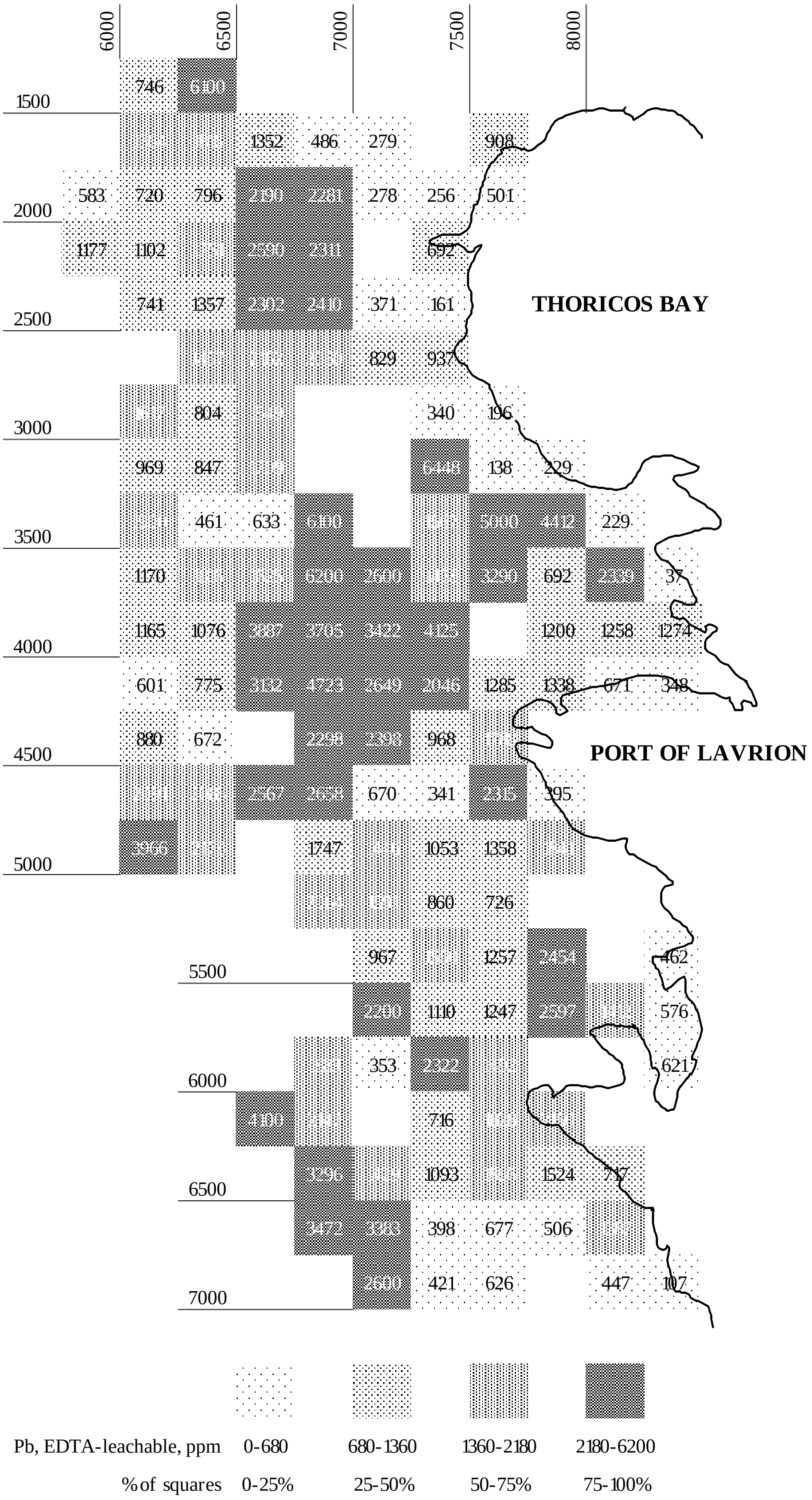


***Figure 2.2.** Distribution of EDTA-leachable Pb in surface soils.*

Correlation between EDTA leachable fraction and total concentration

Twenty samples covering a wide range of contamination were analysed for total concentrations. The correlation between the EDTA leachable fraction of metals and total concentration is shown in figure 2.3.

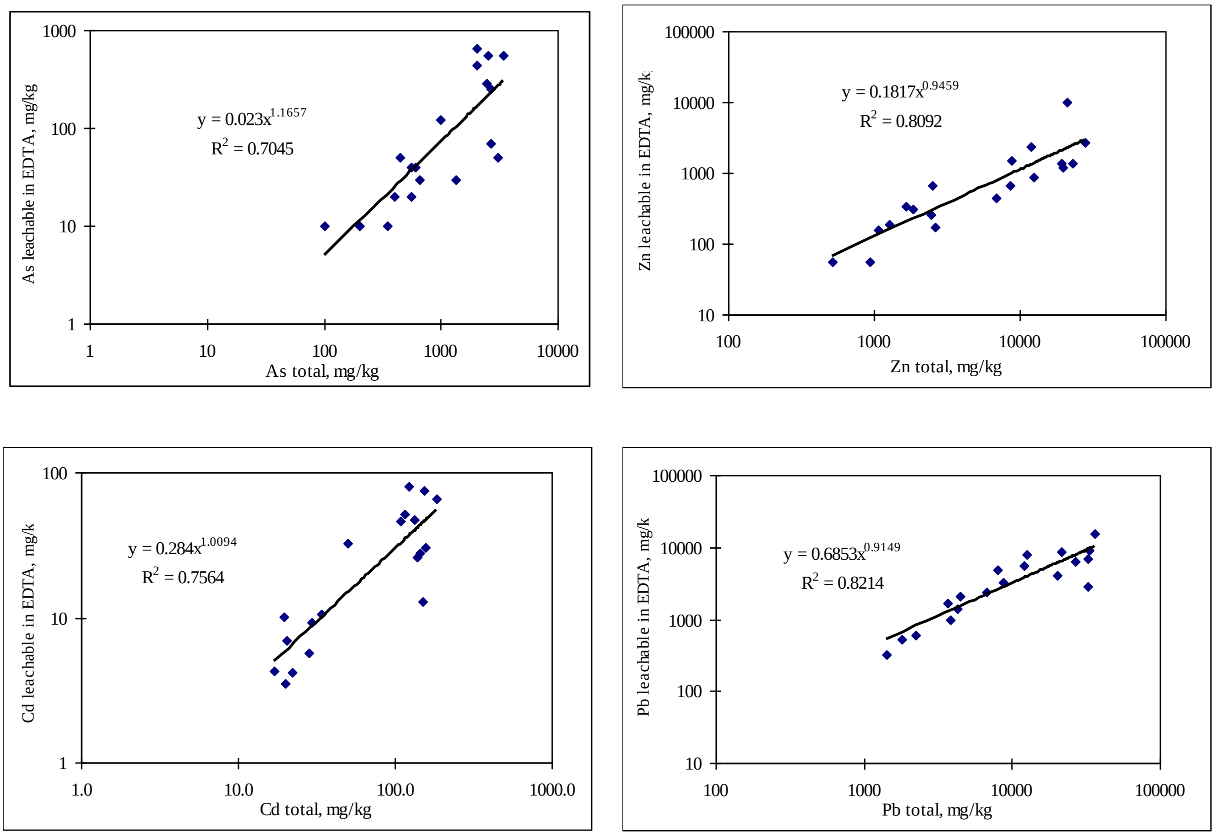


Figure 2.3. *Correlation between EDTA leachable fraction and total concentration of metals*

2.4.3 Toxicity and speciation tests

Toxicity

The twenty samples analysed for total concentration were also subjected to the TCLP testing. The results are presented in table 2.11. Seven of the examined soil samples were found to exceed the EPA toxicity limit for Pb and five for Cd. The samples are characterized as non-toxic with respect to Zn and As. Zinc is leachable in the TCLP solution, but the concentrations remain below the limit of 500 mg/L. Finally, arsenic was found to be quite immobile, with concentrations below the AAS detection limit for most of the samples examined.

The correlation between TCLP leachability and total concentration for Pb, Zn, and Cd is shown in figure 2.4. Based on these correlations, soils containing more than 11400 mg/kg total Pb, 61700 mg/kg total Zn and 136 mg/kg Cd could be classified as toxic following the TCLP test. These values correspond approximately to 25%, 1% and 10% of the area examined, considering the spatial distribution of total Pb, Zn and Cd (Vol.2 maps 3.4, 6.30 and 6.9)

Table 2.11 Application of the TCLP test to Lavrion soils

Sample No.	mg/L in the leachate			
	Pb	**Zn**	**Cd**	**As**
3	**87.9**	63.9	**2.82**	< 2
38	0.5	6.2	0.32	2
53	1.2	19.4	0.52	< 2
79	1	7.3	0.84	< 2
80	0.5	2.0	0.24	< 2
110	0.9	58.5	0.6	< 2
193	**37.7**	152.4	**1.31**	< 2
236	1.3	0.86	0.17	< 2
274	**11.9**	68.3	1.01	<2
275	1.4	11.1	0.23	< 2
279	**34.6**	75.9	0.41	< 2
421	0.5	0.35	0.08	< 2
470	2	6.7	0.25	< 2
492	**132.1**	176.2	**2.17**	< 2
501	**26.6**	35.8	**1.09**	< 2
558	**34.3**	125.9	**1.5**	< 2
561	0.5	3.78	0.12	<2
583	0.5	0.17	0.08	< 2
661	4.7	10.0	0.3	< 2
700	0.9	1.83	0.16	< 2
Toxicity limits	**5.0**	**500**	**1.0**	**5.0**

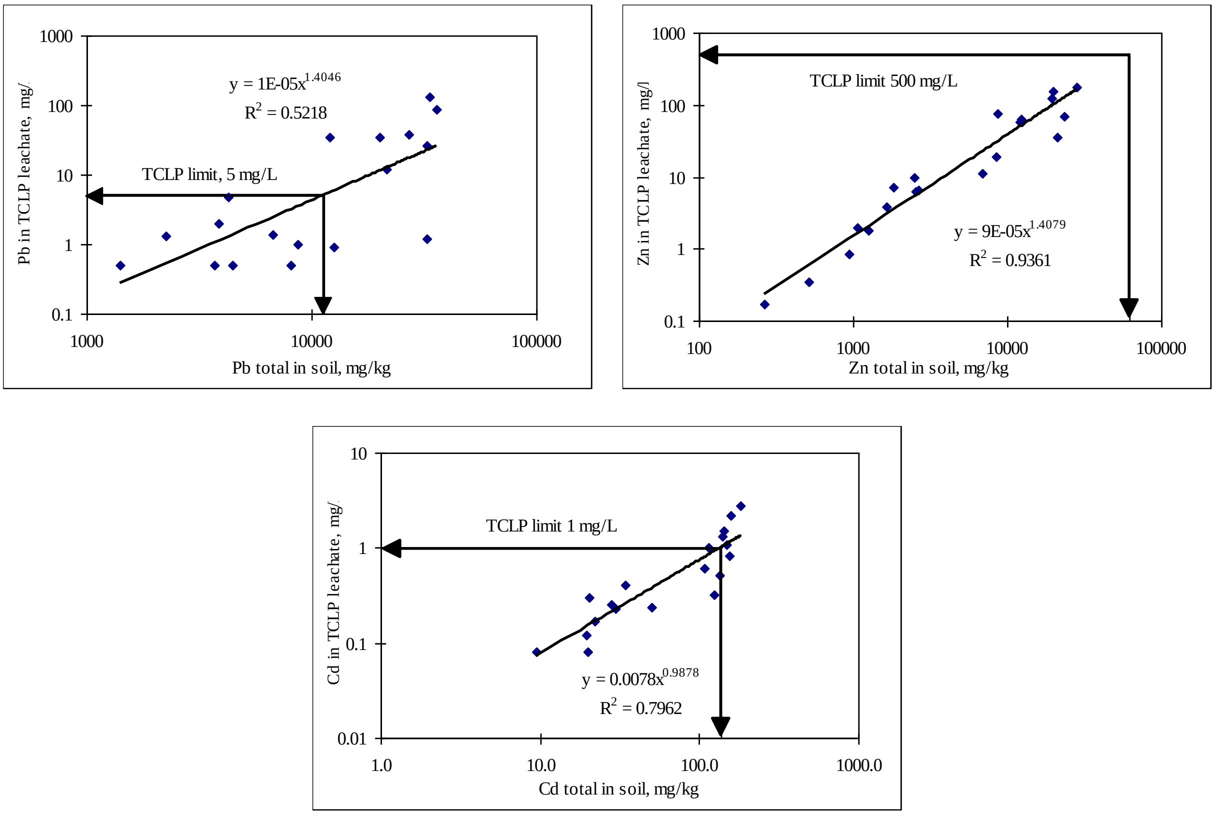


Figure 2.4. *Correlation between TCLP leachability and total concentration for Pb, Zn and Cd.*

Speciation and mobility of metal contaminants

The set of twenty samples was analysed with the sequential extraction technique. The distribution of Pb, Zn and Cd in the five fractions is shown in figure 2.5. The *exchangeable fraction*, which represent the most mobile and hazardous metal species, is very low for Pb and Zn but considerably high for Cd, *i.e.*, up to 50% for some samples. The *carbonate* fraction, which is also considered bioavailable, increases with the total concentration of contaminants and can reach high percentages, *i.e.*, 45% for Pb, 25% for Zn and 40% for Cd. A high percentage of Pb and Zn is also found in the *reducible* fraction. This fraction represents the metal ions, which are adsorbed or coprecipitated on the Fe-Mn oxides of the soil. These species are expected to be released under reducible environmental conditions. It is worthwhile to notice that As was all recovered in the *residual* fraction, which represents the inert form of metals, which are not expected to be released under the conditions normally encountered in nature.

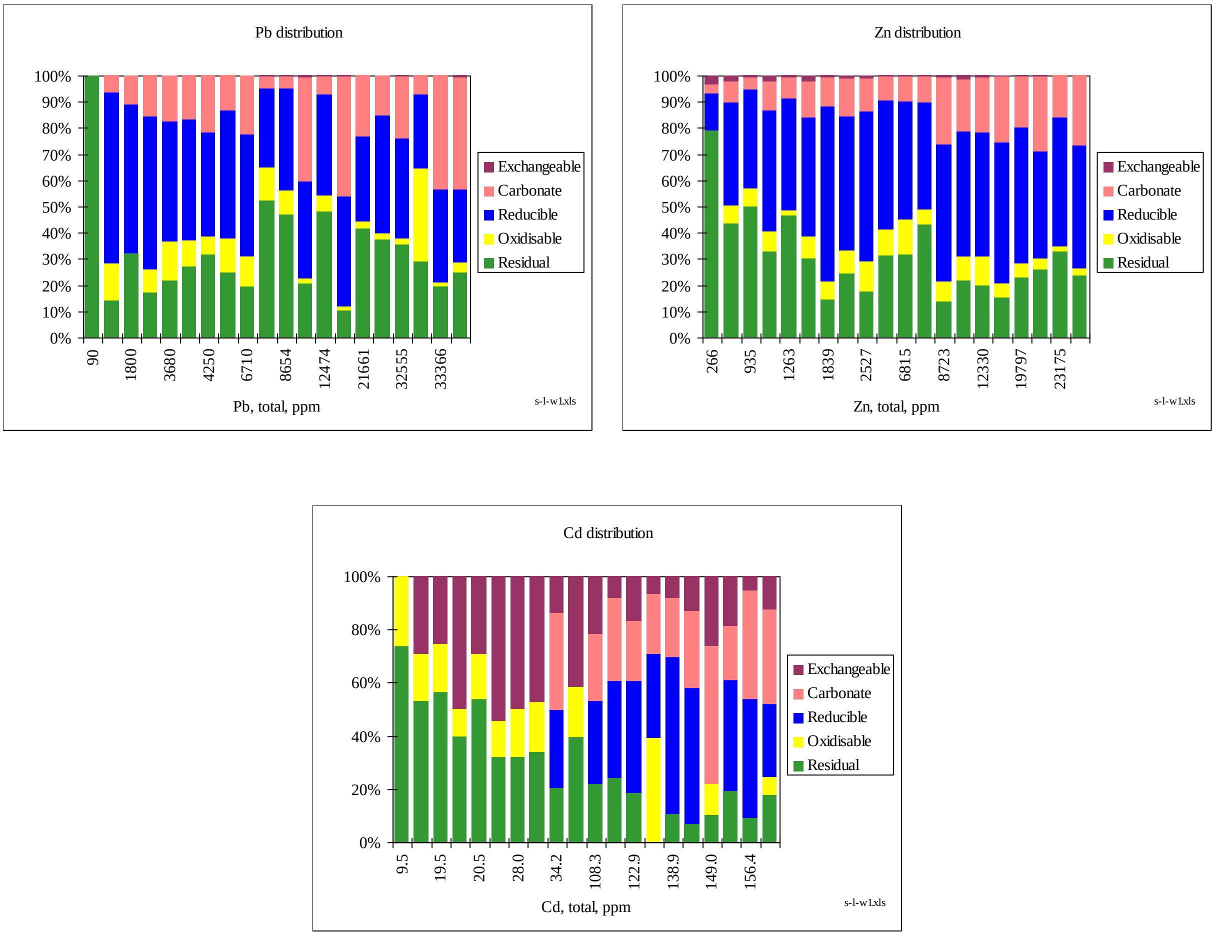


Figure 2.5. *Distribution of Pb, Zn and Cd in the five fractions of the sequential extraction technique.*

2.4.4 Plant sampling and analyses

Vines and olive trees are commonly cultivated in Lavrion area. In order to evaluate directly the phytoaccumulation of toxic elements and the corresponding risks for humans, leaves and fruits from these plants and surface soil around each plant were collected and analysed for Pb, Zn, Cd and As. Sampling was carried out on three fields, containing both vines and olive trees. The two fields (1 and 2) are located on the top of Savoura washing tailings (spoil E), where contamination is very high, and the third field (3) corresponds to an area of relatively low contamination. The results are presented in table 2.12 in comparison with existing guidelines and recommendations for leafy vegetables and fruits.

Table 2.12: Metals uptake by vines and olives (natural weight)

Vines

			Plant tissue [1,2]		**Guidelines** [2]	
	Field	**Soil** [1] mg/kg	**Leaves** mg/kg	**Fruit** mg/kg	**Vegetables** mg/kg	**Fruits** mg/kg
Pb	1	25770	35.2	0.22	0.3 [a]	0.1 [a]
	2	24340	15.5	0.16		
	3	1378	0.33	0.11		
Zn	1	21910	37.1	0.87	5 [b]	5 [b]
	2	21780	18.7	0.78		
	3	396	6.9	0.45		
Cd	1	159	0.60	0.06	0.2 [c]	0.03 [c]
	2	178	0.09	0.03		
	3	2.5	0.03	0.03		
As	1	2049	3.35	0.07	0.2 [b]	0.2 [b]
	2	2078	2.06	0.05		
	3	104	0.15	0.005		

Olives

			Plant tissue [1,2]		**Guidelines** [2]	
	Field	**Soil** [1] mg/kg	**Leaves** mg/kg	**Fruit** mg/kg	**Vegetables** mg/kg	**Fruits** mg/kg
Pb	1	23540	66.4	1.13	0.3 [a]	0.1 [a]
	2	22240	72.6	0.87		
	3	1050	1.9	0.62		
Zn	1	26630	92.7	11.7	5 [b]	5 [b]
	2	22820	50.0	10.6		
	3	375	17.9	7.9		
Cd	1	200	0.96	0.57	0.2 [c]	0.03 [c]
	2	161	0.32	0.46		
	3	2.7	0.77	0.49		
As	1	1936	5.34	0.42	0.2 [b]	0.2 [b]
	2	1748	30.4	0.13		
	3	137	0.96	0.56		

[1] Mean value of 10 samples for soil and plant tissues

[2] Concentrations refer to the natural weight, without drying. Leaves and fruits are washed using detergent.

[a] European Commission recommendations for leafy vegetables and fruits

[b] Greek guidelines for exported vegetables and fruit juices

[c] Guidelines for leafy vegetables and fruits in Belgium, Netherlands and Luxembourg

As seen in the table, the toxic elements are accumulated mainly in the leaves. Vine leaves, which are edible in Greece, contain Pb, Zn, Cd and As above existing guidelines for leafy vegetables. Lead and Zn concentrations in the leaves are above the limit values even in the field of low contamination.

Concerning fruits, risks for human health are more serious for olives, where concentrations exceed guidelines for all four elements. Grapes accumulate mainly Pb at values exceeding guidelines.

Amongst the four elements examined, Pb represents the key–contaminant regarding risks from food intake. Lead concentrations in plant tissues exceed the limits up to 100 times for leafy vegetables and 10 times for fruits.

The above values correspond to the net phytoaccumulation of toxic elements and they were determined applying the washing protocol, as suggested in the *Soil and Plant Analysis* Handbook, *i.e.* thorough washing using detergents in order to remove adhered soil particles. The real intake of toxic elements by humans through food consumption is much higher. A comparative analysis was carried out applying two different washing procedures, *i.e.*, using detergent and using only water as commonly practiced. Measured concentrations were about 10 times higher in the samples washed only with water.

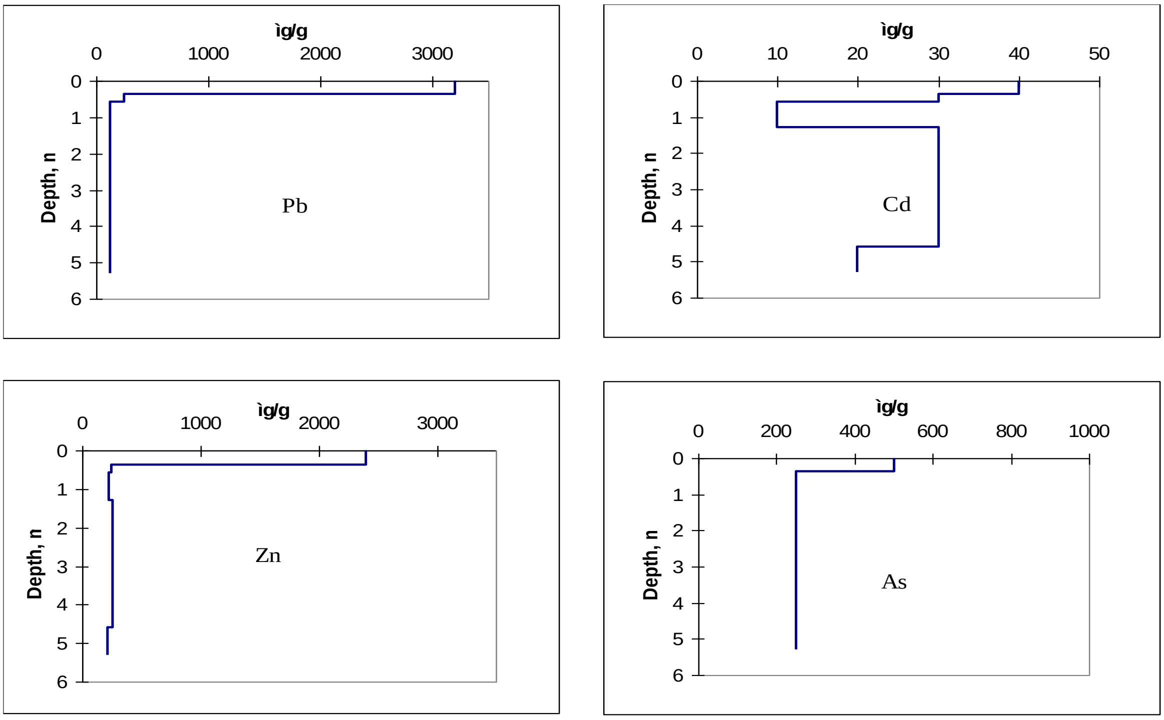
Considering the four categories of contaminated matrices identified in Lavrion, *i.e.*, sulphides, carbonates, slags and soils, introduction of toxic elements in the food chain through phytoaccumulation is a risk only for carbonates and soils. Vegetation is not sustained on the sulphidic tailings due to their low pH (pH<3). Slags finally are completely inadequate for plant growth due to their vitreous matrix and coarse texture.

2.4.5 Depth of contamination

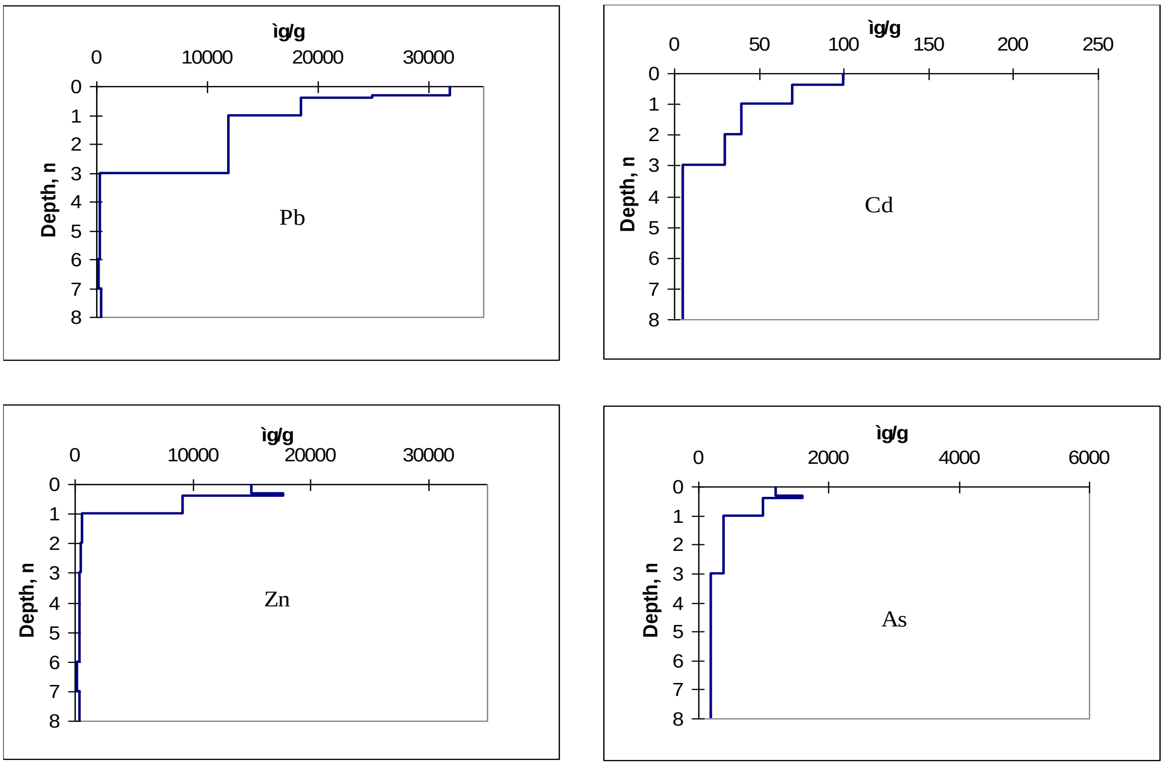
The depth of contamination was evaluated from drill-core samples at 23 locations (fig. 2.1). Detailed data are given in Appendix A2. The results are summarised in table 2.13. Based on Netherlands Intervention values, the depth of contamination varies from several centimeters, *i.e.* G17, G18, G21, to more than 15 meters at several waste disposal sites. It is noted that boreholes G1 to G12 correspond to waste disposal areas and in most cases drilling has not reached the natural soil background. Slags and beneficiation tailings were also detected in many drillcore samples from boreholes G13 and G23, which were drilled outside the typical boundaries of the wastes.

Table 2.13 Maximum depth where the concentrations of Pb, Zn and Cd exceed Netherlands Intervention values

	Pb	**Zn**	**Cd**		**Pb**	**Zn**	**Cd**
Netherlands Intervention values, mg/kg	***530***	***720***	***12***	***Netherlands Intervention values, mg/kg***	***530***	***720***	***12***
Boreholes	**Depth of contamination, m**			**Boreholes**	**Depth of contamination, m**		
G1	>4.3	>4.3	>4.3	G12	>10.0	>10.0	>10.0
G2	>5.0	>5.0	>5.0	G13	15.3	>17.2	>17.2
G3	>6.6	>6.6	>6.6	G14	3.5	2.5	1.8
G4	>7.8	>7.8	>7.8	G15	2.5		
G5	>6.5			G16	4.0	5.0	4.0
G6	7.4	>7.4	>7.4	G17	0.4	0.4	4.5
G7	3.5	3.5	>5.0	G18	1.0	1.0	<0.4
G8	>15.0	>15.0	>15.0	G19	2.5	2.5	2.5
G9	9.3	9.3	9.3	G21	<0.3	<0.3	<0.3
G10	>15.4	>15.4	>15.4	G22	9.0	2.5	1.3
G11	>6.7	>6.7	>6.7	G23	3.0	2.0	3.0



G17



G23

Figure 2.6. *Typical profile of contaminants at two locations in the south (G17) and north (G23) edge of Lavrion city.*

Figure 2.6 shows the profile of contaminants at two locations in the south (G17) and north (G23) edge of Lavrion city. The shallow profiles at site G17 suggest that contamination has resulted mainly from atmospheric deposition of contaminated particles. Pb and Zn were retained at the upper 40cm without any indication of downward mobilisation. On the contrary there is an indication that Cd is washed out from surface soil and transferred to deeper horizons, under the action of infiltrated rainwater. This is in agreement with the sequential extraction results, which have shown that the exchangeable (water soluble) fraction is very low for Pb and Zn and elevated for Cd. Contamination at site G23 (northern edge of Lavrion city) is very high at surface soils, *i.e.* 30,000 mg/kg Pb, and extents to a low depth of 3 meters approximately. It is difficult to attribute the contamination depth to the vertical migration of contaminants through solubilisation in natural waters. Most probably contaminated material has been deposited there or transferred from other waste disposal sites. It is noted that an ancient beneficiation plant has been discovered in the vicinity of site G23.

2.5 Evaluation of environmental risks

The crucial environmental parameters for Lavrion spoils and soils are summarised in tables 2.14 through 2.15 focusing on the following aspects:

a) capacity for generating acidity,
b) quality of pore and run-off waters,
c) total concentration of toxic elements and bioavailability of contaminants and
d) toxicity as estimated with the TCLP test.

Emphasis is given to the particular environmental risks associated with each type of material in order to define the required remedial measures.

2.5.1 Sulphidic tailings

The acid drainage generation is one of the most important problems at the international mining industry and is related with the existence of sulphide compounds in the tailings. The sulphide minerals contained in the spoils are naturally oxidised under the action of meteoric water and atmospheric oxygen and this results in the production of sulphuric acid:

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \xrightarrow{\text{Bacteria}} Fe(OH)_3 + 2\ H_2SO_4$$

Acidity enhances the dissolution of toxic metals and their subsequent migration in the surrounding soils and the aqueous receivers. The high acid generation potential of the sulphidic tailings in Lavrion and the relative dissolution of toxic metals in the acidic waters are shown in tables 2.14 and 2.15.

Sulphidic wastes contain also an appreciable amount of bioavailable metals and they are characterized as toxic following the TCLP test (tables 2.16 and 2.17). It is pointed out that the observed "biovailability" and "toxicity" is due to the partial oxidation of the material. The common sulphide compounds of toxic elements, *i.e.* $FeAsS$, PbS, ZnS, CdS, are not soluble in water. On the contrary, the corresponding oxidation products are partially, *i.e.* $FeAsO_4.2H_2O$, $PbSO_4$, or highly soluble, *i.e.* $ZnSO_4$, $CdSO_4$. The "toxicity" of the material is directly related with the presence of the above oxidation products.

Summarizing the above discussion environmental risks related with the existence of sulphidic tailings include:

- Generation of acidic contaminated waters and water transfer of contamination to the adjacent soils
- Air transfer of contaminated particles, which are inhaled by humans or deposited in the soils.

Table 2.14.

The balance between acid generating and alkaline minerals in Lavrion spoils and soils.

		Acid Generating Minerals		*Alkaline Minerals*	*Balance*	*Paste pH*
		S_t	MAP	NP	NNP	
		%	kg $CaCO_3$/t	kg $CaCO_3$/t	kg $CaCO_3$/t	
Wastes						
Sulphides	A	8.6	269	70	*-199*	2.7
	B	7.7	241	-7	*-248*	6.5
	C	8.2	257	138	*-119*	5.07
	D	31.9	996	-17	*-1013*	2.15
Carbonates	E	1.2	38	600	+562	8.21
	F	1.0	31	200	+169	8.65
Soils						
Borehole	G17	<0.3		210	+210	8.25
	G23	<0.3		313	+313	8.30

Table 2.15

Quality of pore and run-off waters (concentration in mg/l)

Lavrion	**pH**	**Pb**	**Zn**	**Cd**	**As**	**Fe**	**SO_4**
Wastes							
Sulphidic							
A (accumulated on surface)	1.9	0.5	760	1.8	43		
A (pore water)	2.5	1.0	5000	20	<2	300	15000
B (pore water)	2.3	3	1300	6	<2	3000	50000
C (pore water)	4.8	3.2	16000	30	<2	3400	40000
D (run-off water)	1.9	0.7	1150	3.9	800	10000	30000
D (pore water)	4.0	2.6	40	0.2	<2	85	1000
Carbonates/Oxides							
E (pore water)	7.0	<0.5	30	0.1	<2	<0.5	400
F (pore water)	7.0	1.7	8	2	<2	<0.5	5000
Municipality Well	7.8	<0.5	0.07	<0.05	<0.5	20	
Specifications							
Disposal to aqueous receivers	6-9	0.1	1.0	0.1	0.5	2	
Drinking water		0.05	5.0	0.01	0.05		

Table 2.16. Concentrations and bioavailability of toxic elements in wastes and soils

Concentrations μg/g of soil (ppm)		**Pb**		**Zn**		**Cd**		**As**	
		Tot.	Bioav.*	Tot.	Bioav.*	Tot.	Bioav.*	Tot.	Bioav.*
Wastes									
Sulphidic	A	4940	400	26000	12200	75.3	50.8	3000	300
	B	4290	270	3180	442	13.2	9.2		
	C	69600	2800	57200	39400	264	190		
	D	9300	3400	1440	300	13.4	6.4	10600	100
Carbonates/Oxides	E	28200	6630	27100	6040	169	56.4	5500	< 50
	F	34900	11900	40400	6070	125	59.6		
Slags	G	10260	290	76700	9600	27	21	250	< 50
Soils									
Low Contamination		2260	350	935	51	22	19	400	<50
Medium-Low Contam.		3860	650	2630	255	28	23	550	<50
Medium-High Contam.		6710	1520	6630	674	29.5	24	600	<50
High Contamination		26900	4150	19800	3910	139	42.4	3050	<50
Netherlands Intervention values		***530***		***720***		***12***		***55***	

* Bioavailable fractions of metals by the sequential extraction test

Table 2.17. Results of the toxicity test (TCLP tests) in wastes and soils from Lavrion

Concentrations mg/l of TCLP leachate		**Pb**	**Zn**	**Cd**	**As**
Wastes					
Sulphidic	A	0.3	645	1.26	<2
	B	1-18	41.5	0.1-4	<2
	C	4.1	2420	10.6	<2
	D	2.9	17.7	0.2	6
Carbonates/Oxides	E	87.9	207.3	2.48	<2
	F	232	185	2.53	<2
Slags	G	<0.3	41.5	0.07	<2
Soils					
Low Contamination		1.3	0.86	0.17	<2
Medium-Low Contam.		0.5	3.8	0.12	<2
Medium-High Contam.		1.4	11.1	0.23	<2
High Contamination		37.7	152	1.31	<2
TOXICITY LIMITS		**5**	**500**	**1**	**5**

Risks for intake of toxic elements by humans through drinking water are minimal, given that Lavrion is connected to the supply network of Athens since 1983. Moreover, water samples from several wells in the area were not found to be contaminated, indicating that groundwater is more or less protected from the calcareous geological formations in the area. A special risk for local human population, mainly children, is the direct contact with the strongly acidic waters which are accumulated on the surface of sulphidic tailings A and D.

Finally, there is no risk for introduction of toxic elements in the food chain. Due to the acidic paste pH, vegetation is very poor on the sulphidic tailings.

The tailings, which are considered to be more hazardous, are:

(a) Bodosakis Beach Pyrites: 120.000 t, D spot in figure 2.1. These tailings exhibit very high potential for generating acidity (1000 kg H_2SO_4 /t). Run-off water accumulated in the area was found to be very acidic with high concentrations of dissolved toxic elements (pH 1.9, Pb 1.7 ppm, Zn 1150 ppm, As 800 ppm). Characteristic pictures of the acidic waters accumulated on Bodosakis pyrites are given in photos 1 in the photographic documentation annex.

(b) Kavodokanos Pyrites: 600.000 t, A spot (fig 2.1.). Even though their acid generation potential is lower than the one of Bodosakis, these tailings are very hazardous because of their position and their volume. Their disposal in a stockpile raised the production of acidic waters (photos 2) and moreover increased the air transportation of pollutants in the city of Lavrion. It is very important to mention that new houses are built year by year on the top of these tailings (photos 3 and 4).

2.5.2 Carbonate tailings

These tailings are characterized as highly toxic following the TCLP test (EPA) (table 2.17 and Figure 2.1) and contain considerable levels of total and bioavailable toxic metals (table 2.16). They occupy an extended area, where public, residential and agricultural activities have been developed. Risks thus include:

- Direct contact of humans with the contaminated material and inhalation or ingestion of contaminated particles
- Consumption of plants with high levels of contaminants

More particularly:

(a) Savoura wastes: 5,000,000 t, E spot. They occupy an extended area of more than 47 hectares all along the west side of Lavrion city. Systematic residential use and small-scale agricultural activities have been developed on the top of these spoils (photos 5). Vines and olive-trees cultivated on the waste E accumulate toxic elements at values exceeding considerably existing guidelines for edible plants. Moreover, air transfer of contaminated particles in not negligible despite the relatively low percentage of fine particles (18% below 63μm). This is due to the loose sandy texture of the material, which favors wind erosion and transfer.

(b) Telmata at Thoricos bay: 1,200,000 t, spot F. They contain up to 35 000 ppm total Pb and approximately half of it is bioavailable (12 000-16 000 ppm). The material is very fine in texture (78% below 63μm) and dust is often generated from this silty loam material due to the dry and windy conditions prevailing in Lavrion. Therefore, direct inhalation and ingestion of contaminated particles by humans constitute high risks for spoil F. It should be noticed that schools and public buildings have been built on the top of these tailings (photo 6).

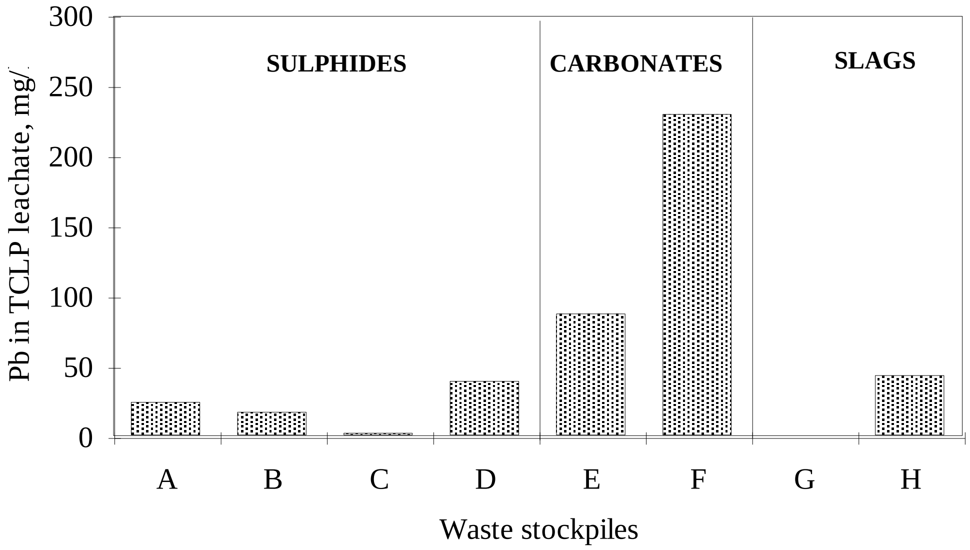


Figure 2.7. *Lead toxicity of Lavrion wastes evaluated with the US TCLP test. Regulatory limit: Pb = 5mg/l.*

2.5.3 Slags

Slags (photos 8) have been considered in the past as inactive and safe for the environment. The present study has showed that partial dissolution of toxic metals could take place, when the big slag pieces are ground to fine particles. However slags are evaluated as less hazardous, compared to the rest tailings of Lavrion. Due to their coarse texture and their hard vitreous matrix, they have infinite water permeability and are not susceptible to wind erosion. Risks for water or air transfer of contaminants are therefore estimated as minimal.

2.5.4 Soils

Based on the *total* concentration of contaminants, the primary metals of concern at Lavrion surface soils are *As* followed by *Pb* and to a lesser extent *Cd* and *Zn*. Arsenic was seen to be quite immobile with all the alternative leaching tests, which were applied to evaluate the mobility and availability of elements. On the contrary Pb was found to be highly leachable. More than 75% of the area examined contains Pb, which is leachable in EDTA at values exceeding the Dutch Intervention values (530 mg/kg) and 25% is characterized as toxic following the TCLP procedure. Phytoaccumulation in grapes and olives was found to exceed the guidelines for edible products, even in soils with relatively low contamination.

The major risks for humans are similar to that prevailing for the carbonate tailings and include the direct contact, ingestion and inhalation of contaminated material and the introduction of contaminants to the food chain (photo 7).

2.6 Selection of remedial technologies

The environmental rehabilitation in Lavrion presumes the development of an integrated strategy, where two major categories of actions will be included:

i) Actions for *isolation / decontamination of active pollution sources*

ii) Actions for *remediation of contaminated soils*

The selection of appropriate technologies for the rehabilitation of wastes and soils should be based on a detailed cost and benefit analysis considering the following criteria:

- Protection of human health and environment.
- Acceptance by the state authorities and the local community.
- Reduction of the volume and the toxicity of wastes.
- Direct effectiveness.
- Long-term effectiveness and duration.
- Applicability.
- Acceptable cost.

The remediation technologies can be classified in four categories according to the methodology that is used to mitigate or eliminate the environmental risks:

Removal of wastes and contaminated soils from the area and controlled disposal to another area.

By this way toxic materials, wastes and soils are removed from the area under rehabilitation and carried to another place where they are disposed under control to a dum properly constructed with impermeable bottom and walls. Land availability, public acceptance and the high cost for the appropriate isolation of the new disposal area, consist the major problems associated with this option.

Isolation techniques.

These techniques include either the surface or the complete isolation of the toxic wastes from the natural environment. The isolation of the hazardous wastes from the atmospheric air and surface waters can be obtained by applying impermeable surface covers. In parallel, the protection of the ground water is faced with the construction of vertical impermeable walls around the volume of the wastes

Techniques for the stabilisation of the pollutants.

The purpose of these methods is to achieve the partial or complete immobilization of the pollutants. Solidification and chemical stabilization are the two main alternatives. The *solidification techniques* (*i.e.*, cementation, vitrification), convert mainly the physical characteristics of the tailings and the soils, encapsulating the pollutants into an inactive solid matrix. The *chemical stabilization techniques* convert the soluble and bioavailable forms of the pollutants into insoluble and inactive substances through mechanisms of precipitation, adsorption, oxidation-reduction, etc.

Techniques for the mobilization of the pollutants.

This category includes all these technologies that remove the pollutants from the matrix of the soils (or the wastes) with the use of proper physicochemical methods. Metals can be removed applying either the classical methods of mineral processing (separation of fine particles, gravity separation, flotation etc.) or leaching techniques with the use of appropriate chemicals such as, mineral or organic acids oxidation/reduction reagents or chelating agents etc.

The complexity of the environmental problem in Lavrion (heterogeneity of pollution sources, mixing of natural soils and wastes etc.) imposes to use a variety of techniques which should be selected according to the particular characteristics of the wastes and soils and the specific environmental risks associated with each type of material. The isolation techniques were considered to be more suitable for eliminating the risks associated with the sulphidic tailings, while chemical immobilization and removal of metals can be more effective when applied for the treatment of oxidic tailings and soils. The initial screening has been based on a comprehensive literature survey concerning the available techniques and the international experience on similar cases. The specific characteristics of the matrices (wastes/soils) and the type of contaminants (key-contaminants, concentration, and speciation) were the guide for this preliminary technology screening. The alternative techniques were then evaluated with small-scale laboratory tests in order to assess their applicability on Lavrion soils and wastes. The most effective techniques were selected for further examination and pilot-scale testing on Lavrion.

Isolation techniques, which were developed and applied on sulphidic tailings, are discussed in Chapter 3. The chemical immobilization technologies are presented in Chapter 4. Finally, Chapter 5 includes the work undertaken for the development of technologies aiming at the removal of contaminants.

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SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION

LIFE Project, Contract No.: 93/GR/A/4/GR/4567

VOLUME 3

ENVIRONMENTAL CHARACTERISATION OF LAVRION SITE – DEVELOPMENT OF REMEDIATION TECHNIQUES

CHAPTER 3

ACID DRAINAGE CONTROL – REHABILITATION OF SULPHIDIC TAILINGS

ATHENS, DECEMBER 1999

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3. ACID DRAINAGE CONTROL - REHABILITATION OF SULPHIDIC TAILINGS

3.1. INTRODUCTION

Within LIFE project, to develop rehabilitation techniques for sulphidic tailings and concentrates encountered at Lavrion City, field tests were performed. Techniques under examination include mixing of highly sulphidic tailings with limestone and isolation of sulphidic tailings with compacted clay or geomembrane cover.

In this chapter the design and methodology followed for the construction of field tests is described. Furthermore, the results of the pilot scale application of the selected techniques after a monitoring period of 2.5 years are presented. Based on the volume and quality of drainage, the effectiveness of the rehabilitation techniques in the inhibition of acid generation from the sulphidic wastes is evaluated. Finally, techniques are compared in terms of their application cost .

3.2. REHABILITATION TECHNOLOGIES-STATE OF THE ART

It is well recognised that acid mine drainage generation constitutes a significant environmental problem associated with base metal, gold and uranium mining operations as well as the coal and lignite mining industry. The sulphide minerals, such as pyrite, FeS_2 and pyrrhotite, $Fe_{1-x}S$ oxidise under the action of oxygen and water and in the presence of the acidophilic bacteria *Thiobacillus ferrooxidans* resulting in the production of low-pH waters loaded with dissolved SO_4^{2-}, iron and other heavy metals and toxic compounds.

Due to the autocatalytic and self-propagating nature of both the chemical and bacterial mechanisms responsible for sulphide oxidation and pollutants migration, the sources for acid mine drainage generation including waste rock dumps, processing tailings, temporary stockpiles of sulphidic concentrates, open-pit and underground mining works may remain active for tens of years after the mine closure. Furthermore, the effects of acid drainage can be both pernicious and far reaching since the contamination of the surface and underground waters may carry the pollution significant distances from the mining area.

Control technology of acid mine drainage includes a) *primary* techniques to prevent the acid generation reactions, b) *secondary* measures to inhibit the migration of acid generation products into the environment and c) *tertiary* control including the collection and subsequent treatment of acidic waters.

Given that acid drainage can be released for decades from an affected site, water collection and treatment methods, usually available in an operating mine, are quite costly to be considered as a long-term option for protecting the downstream environment in the post-mining period. Instead, preventive action for the long-term control of acid generation process is a far preferable strategy, especially when planning new waste management facilities. The primary control techniques developed so far to prevent the acid generation process in mine/milling waste disposal facilities aim to restrict the principal components of the acid generation process, *i.e.*, separation and isolation of sulphide bearing wastes, elimination of water and oxygen. Moreover, preventive methods aim to control the factors that largely affect the nature and extent of acid formation, including water pH, bacterial activity, dissolved ferric iron and temperature, Draft of ARD, (1989), Ritcey, (1989). The main techniques used to prevent acid generation from mine/milling waste disposal facilities are given in Table 3.1.

Table 3.1. Techniques to prevent Acid Mine Drainage formation

Draft of ARD (1989)

Techniques	Objective of control
Treatment of sulphidic wastes	Sulphide removal or isolation
Alkaline additives *(Carbonates/phosphates/silicates)*	pH control, Fe^{3+} control stabilisation of sulphides
Bactericides	Control of bacterial action
Water cover	Exclusion of oxygen
Dry covers *(soils and/or synthetic membranes)*	Exclusion of water and oxygen

The applicability and effectiveness of any technique to control acid generation depends on a number of case specific parameters. Criteria that need to be considered in the selection of preventive measures include:

- ✓ *site conditions* such as climate,
- ✓ topography and hydrogeology,
- ✓ *waste characteristics* such as acid generation potential, particle size, permeability,
- ✓ *short and/or long-term effectiveness* of the preventive action and
- ✓ *environmental sensitivity* to acid mine drainage, Draft of ARD (1989).

Water is probably the most effective and readily available cover for limiting the oxygen transfer and controlling acid generation in reactive wastes (Mine Environmental Neutral Drainage, MEND project 2.35.2b, January 1997). The effectiveness of water covers is mainly attributed to the very low diffusion coefficient and low solubility of oxygen in water, equal to $2x10^{-6}$ cm^2/sec and 8.6 g/m^3 at 25 °C respectively. However, water cover has limited applicability in regions with long dry periods such as Greece. In dry climates, alternative techniques such as dry covers and alkaline additives may be preferably applied for the inhibition of acid generation from existing stockpiles of sulphidic wastes.

Dry covers

A variety of materials including *soils, synthetic membranes, asphalt, concrete, geopolymers* etc. have been effectively used as dry covers. The aim of this control technique is to reduce oxygen and water penetration into the sulphidic wastes and minimize the generation of leachates. The properties of a variety of materials used as dry covers are summarised in Table 3.2.

A *soil cover* should have a low hydraulic conductivity and must retain a high degree of saturation in order to effectively prevent water and oxygen transfer into the potentially acid generating wastes. Soils with low hydraulic conductivity include clays, silty clays, clayey and silty sands whereas commercial bentonite can be added to coarser textured soils to reduce their water permeability to below, *i.e.*, <1 x 10^{-7} cm/sec.

One of the most appealing techniques for the construction of soil covers relies on the use of natural soils to generate a capillary barrier system where a saturated, fine grained soil layer with a low hydraulic conductivity is placed between two coarse grained material covers. The middle layer will tend to maintain a high water content while the coarse material will dry more easily, Nicholson, (1989). Field performance of this type of cover has been documented at a number of sites with wet climate, *i.e.* where annual precipitation equals or exceeds the potential evapotranspiration. Covers recently designed for application at sites with dry climate, *i.e.* where annual precipitation is low, *i.e.* less than 300 mm/year and potential evapotranspiration is high, *i.e.* 700 mm/year, are referred as store-and-release covers. These "dry site" covers do not incorporate a low permeability compacted layer; they store infiltrating water in the root zone long enough to allow evapotranspiration to remove water before it infiltrates into the waste, Swanson *et al.* (1997).

Table 3.2. Characteristics of materials used in the construction of covers Draft of ARD, (1989)

Cover material	Water permeability (m/sec)	Advantages / Disadvantages
Compacted clay	10^{-9} - 10^{-11}	- Available in large quantities. - Good sealing if it is protected and maintained. - Cracking, erosion and root penetration may occur.
Compacted till	10^{-7} - 10^{-9}	- As above but with higher permeability.
Compacted topsoil	10^{-5} - 10^{-8}	- As above but less robust and more permeable.
Peatland bog	10^{-5} - 10^{-6}	- Need to maintain in saturated condition. - Impractical for elevated waste dumps and side slopes.
Concrete	10^{-10} - 10^{-12}	- Subject to cracking, frost and mechanical damage.
Asphalt	10^{-20}	- As above
HDPE synthetic	Impermeable	- Requires proper bedding and protective cover. - Subject to root and mechanical penetration.

Critical parameters in the construction of engineered soil covers include physical properties of the soils such as particle size distribution, water content, Atterberg limits, size of clods, hydraulic conductivity as well as technical parameters including energy of compaction and bonding of lifts, EPA/625/4-91/025. Soils may be damaged by excessive differential settlement, desiccation and other environmental stresses.

Polymeric geomembranes or flexible membrane liners (FMLs) used for the construction and isolation of municipal landfills are recently employed in the construction of mine waste disposal facilities. Polyethylene (PE) is probably the most common synthetic lining material, either as high density polyethylene (HDPE) or less commonly low density polyethylene (LDPE) whereas polyvinyl chloride (PVC) may also be used. Critical parameters in the design of a geomembrane cover in a waste disposal facility include vapor transmission, biaxal stresses via subsidence and planar stresses mobilized by friction, EPA/625/4-91/025.

Durability and aging of geomembranes have to be taken account, especially when the long-term performance of the cover in the post closure period is assessed. Degradation processes such as ultraviolet radiation are prevented by burying the geomembrane in soil soon after installation; chemical degradation is negligible since the geomembrane is placed in contact with water and not leachate as is the case for the liner placed below the waste. However, long-term oxidation of geomembranes is a degradation mechanism that can only be retarded, via antioxidants, but not eliminated, and consists a focal parameter for experimental modeling, EPA/625/4-91/025.

It is noted than the U.S. Environmental Protection Agency (EPA/625/4-91/025) recommends that after the decommissioning of a hazardous waste management unit, the final cover, illustrated in Figure 3.1, should consist of:

1. A *low hydraulic conductivity geomembrane / soil layer:* A 60 cm layer of compacted natural or amended soil with a hydraulic conductivity of 1 x 10^{-7} cm/sec in intimate contact with a minimum 0.5 mm geomembrane liner.

2. A *drainage layer:* A minimum 30 cm soil layer having a minimum hydraulic conductivity of 1 x 10^{-2} cm/sec, or a layer of geosynthetic material having the same characteristics.

3. A *top, vegetation/soil layer:* A top layer with vegetation and a minimum of 60 cm of soil graded at a slope between 3 and 5%.

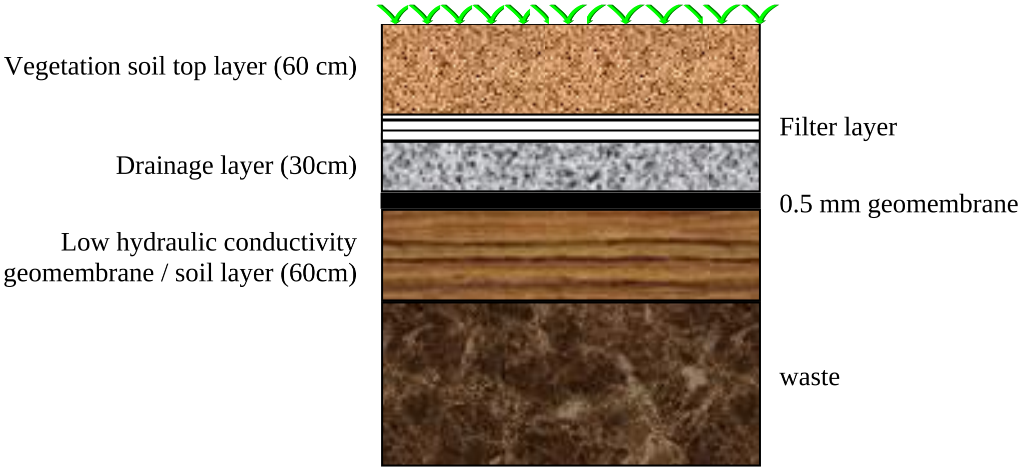

Figure 3.1. *EPA-recommended landfill cover design.*

The cost associated with large-scale mining application is the limiting factor for the extensive use of the various materials proposed as mining covers. Although both synthetic and natural covers may be cost-effective when applied in relatively small disposal areas, they may not be feasible for the large disposal facilities, typical in the mining industry. Thus, further research studies have been performed for the potential use of other readily available, inexpensive and potentially non-phytotoxic, non-polluting waste products including depyritized tailings, granulated slags and fly ash produced from the lignite fired power plants and/or waste incineration stations. Making use of waste products is not only very economical, but it also eliminates the need for the safe environmental storage of these materials. However, these wastes often contain potentially toxic substances, which may inhibit plant growth or may eventually leach into the surrounding environment.

Alkaline additives

Alkaline additives are considered as a viable method for the control of acidic drainage from sulphidic waste disposal areas. The concept of blending acid producing rocks with calcareous material already existing in the overburden strata constitutes the simplest form of alkaline addition. Studies in the Appalachian coal region suggest that "if neutralising materials are in excess of 3:1 (chemically) over the acid-producing ones or if the sulphide-bearing materials represent less than 10-15 per cent (volume) of the total section, then blending may be the most viable alternative", Sturm, (1987). Given that in most waste deposits the amount of highly reactive neutralising minerals do not often balance the potential acidity of the contained pyrites, external addition of alkaline materials to maintain the pH in the neutral range is considered as a feasible control alternative.

Additives including *lime*, *limestone*, *sodium carbonate*, and *NaOH* have been reported to effectively prevent acidic drainage, Heltz *et al.*, (1987), Day, (1994), Draft of ARD, (1989). Industrial by-products including *phosphatic slimes* and *alkaline siliceous materials* such as *fly ash* were also seen to inhibit acid generation, Watkin and Watkin, (1983), Chiado et. al., (1988), Renton, (1988), Meek, (1994). Major parameters dictating the effectiveness of base additives are the acid neutralising capacity, and the contact of acidic material with neutralisers and water, Draft of ARD, (1989).

The potential of limestone to prevent acid generation has been well recognised from the fact that in sulphides and coal mines containing abundant natural limestone or other carbonate minerals, limited if any acidity is formed. In sulphidic waste stockpiles when calcite is present, the overall oxidation-neutralisation reaction depends on pH, Morin and Hutt, (1994):

pH<6.4

$$FeS_2(s) + 2CaCO_3(s) + 3.75O_2(g) + 1.5H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 2Ca^{2+} + 2CO_2(g) \quad (1)$$

pH>6.4

$$FeS_2(s) + 4CaCO_3(s) + 3.75O_2(g) + 3.5H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 4Ca^{2+} + 4HCO_3^{-} \quad (2)$$

Upon neutralisation of the acid produced during the oxidation of pyrite, a protective ferric oxy-hydroxide layer would accumulate around the pyrite grains, thus impairing its further dissolution, Nicholson, (1990). According to field studies, the presence of carbonates in sulphide tailings may enhance the formation of hardpan layers on the stockpile surface consisting of oxidation products such as ferric hydroxide and gypsum that would act as an oxygen and water diffusion barrier (Blowes *et al.* 1991).

The recommended alkaline addition rates have been the subject of much controversy. According to the conventional Acid Base Accounting method, (ABA; Sobek *et al.* 1978), the amount of $CaCO_3$ that must be added to prevent acid generation is determined by the *Net Neutralisation Potential, NNP* (kg $CaCO_3$/t) of the waste under study. NNP is calculated by subtracting *Maximum Potential Acidity, MPA* (kg $CaCO_3$/t) from *Neutralisation Potential, NP*, (kg $CaCO_3$/t). MPA is calculated by the weight percent sulphur multiplied by 31.25 according to the stoichiometry of reaction (1), *i.e.* 1 mole of pyrite is neutralised by 2 moles of calcite. Based on field studies, piles of acid producing rock amended with limestone at a

NP/ MAP ratio of 1.0 produced a circumneutral drainage after 11 years of monitoring, (Donovan and Ziemkiewicz 1994).

However, other researchers support that with ABA, the $CaCO_3$ required to supplement deficient NNP may be underestimated due to the presumption that CO_2 will ex-solve, according to reaction (1). Considering that the prevailing neutralisation process is described by reaction (2), it is suggested that for the neutralisation of 1 mole of pyrite, 4 moles of calcite are required (Cravotta *et al.* 1990). Monitoring data for a number of reclaimed surface coal mine sites in Pennsylvania, revealed that the NNP measurement provided a safe prediction of the drainage water quality (*i.e.*, net acidic / alkaline water) when the MPA of the overburden was computed according to the stoichiometry of reaction 2, *i.e.* by multiplying total S, in weight percent, by 62.5, Brady *et al.*, (1990). In agreement with the above results, laboratory tests in stockpiles of acid generating rock (2.1 % S) indicated that the actual quantity of limestone required to prevent acid drainage in perpetuity would probably be at least twice that determined by conventional acid-base accounting, Day, (1994).

On the other hand, limestone added in small amounts, *i.e.*, 3 and 10% of the stoichiometrical quantity to waste rock containing 9.5% S from Heath Steele mine, Canada resulted in a significant reduction of acid production by 83% and 98% respectively for a period of 3 years (Payant *et al.* 1995).

The contradiction of the above results may be attributed to the variability in the physical and geochemical characteristics of the sulphidic wastes under study, the distribution and exposure of the acid-generating or neutralising materials, the hydrogeological variability as well as the restricted capability of the experimental techniques used to accurately predict the long-term on-site performance of the different preventive techniques examined. When correctly engineered, alkaline additives systems may yield an efficient waste management solution without the long-term liability and maintenance of artificial structures such as dry covers and artificially flooded impoundment.

3.3. DEMO-SCALE APPLICATION OF SELECTED REHABILITATION TECHNIQUES

3.3.1 Selection of technologies

For the selection of the rehabilitation techniques to be tested in the field applications, the following were considered:

- literature data on the cost-effectiveness of techniques in preventing acid generation from sulphidic wastes/ applicability of techniques in Greece, and
- laboratory studies performed by NTUA on the influence of limestone in the acid generation rate of a pyrite concentrate material.

Based on the literature review, application of dry covers constructed either from natural low permeability soils or synthetic materials is considered an effective measure in preventing the production of acidic drainage from existing stockpiles of sulphidic wastes. The performance of dry covers has been relatively well tested both in the laboratory and in the field. A geomembrane layer has been recommended as the preferred barrier system in a typical solid waste landfill (Daniel, 1995). The effectiveness of this technique depends on construction quality assurance parameters rather than site characteristics such as climate, however the cost of application may be quite high. On the other hand, the application of a natural low permeability soil has reduced cost, however climatic factors would significantly affect its performance. It is noted that available data refer to the application of dry covers in USA and Canada and little experience exists on the long-term effectiveness of technique when applied in climates with pronounced dry seasons.

Within the above framework, for Kavodokanos sulphidic tailings of Lavrion, pilot scale application aimed to comparatively examine the performance of two cover systems consisting of different barrier layers, *i.e.*, geomembrane HDPE and compacted clay.

The application of limestone is also a low cost and effective alternative technique for inhibiting acid generation from sulphidic wastes. Most of the recent applications of limestone refer to the amendment of wastes containing 1-10 % S (Heltz *et al.* 1987; Day 1994; Rose and Daub 1994; Dave and Vivyurka 1994; Payant *et al.* 1995). However, based on lysimeter kinetic tests performed in the laboratory of Metallurgy, limestone addition could be also effectively applied in the reduction of acid generation rate from highly sulphidic wastes. Mixing pyrite containing 47% S with limestone in an amount corresponding to only 5% of the contained acidity, resulted in the production of drainage with near neutral pH. Under these conditions, ferric iron precipitated and iron levels in solution remained below detection limit (*i.e.* <0.2 mg/l). Continuous dissolution of limestone in response to the acid generation prevented the formation of acidic drainage. Furthermore, based on drainage quality and analysis of the solid residues of lysimeters, limestone addition reduced the rate of pyrite oxidation by 53%. It was deduced that limestone homogeneously mixed with the pyrite concentrate in an amount of 75 kg $CaCO_3$/t would effectively inhibit acid drainage generation in the disposal area for a 2.5 year period.

Based on the findings of the laboratory study, for Bodosakis highly pyritic material (50% FeS_2) disposed at Lavrion, the pilot scale application involved homogeneous mixing of the pyrite material with limestone sand in amount corresponding to a low percentage of the stoichiometric quantity. Alkaline addition at a ratio considerably lower than the stoichiometric requirement would not sufficiently neutralise the acidity produced from the pyrite material in the long term, however dissolution-precipitation reactions involved in the system may result in cementing together the particles, forming a low-permeability layer (hard pan) that would inhibit further oxidation of pyrite.

3.3.2 Design and construction of the field tests

Four 25 by 25 m test plots were designed as follows:

- Test 1- Isolation of Kavodokanos Pyrites with a geomembrane cover
- Test 2- Isolation of Kavodokanos Pyrites with a low permeability clay cover
- Test 3- Homogeneous mixing of Bodosakis Pyrites with limestone
- Test 4- Control area

A plan view of the study area is shown in Figure 3.2.

The test pad was constructed in the Kavodokanos pyrites stockpile. The first action undertaken was to level off the surface of the stockpile. Then the testpad was subdivided into equal quadrants by placing a 2 mm HDPE liner (photos 9 in the photographic documentation annex). A cone shaped lysimeter with 10 m diameter and 1.5 m height was constructed in the center of each quadrant using a 2 mm HDPE geomembrane (photos 10,11). Each lysimeter was filled with Kavodokanos pyrite material, which was excavated during preparation of the study area and had characteristics similar with those given in Table 3.6. It is noted that the material was already oxidised resulting in negative Neutralisation Potential values, (*i.e.*, -7.5 to -22.5 kg $CaCO_3$/t and NNP value of material averaged to -405 (±26) kg $CaCO_3$/ t). The quantity of sulphidic tailings placed in each lysimeter is estimated to 40 m^3 corresponding to 61 dry tonnes. For the collection and monitoring of pore/ drainage water, the lysimeter was connected to a lysimeter sample collection chamber by means of a PVC drainpipe with a diameter of 100 mm.

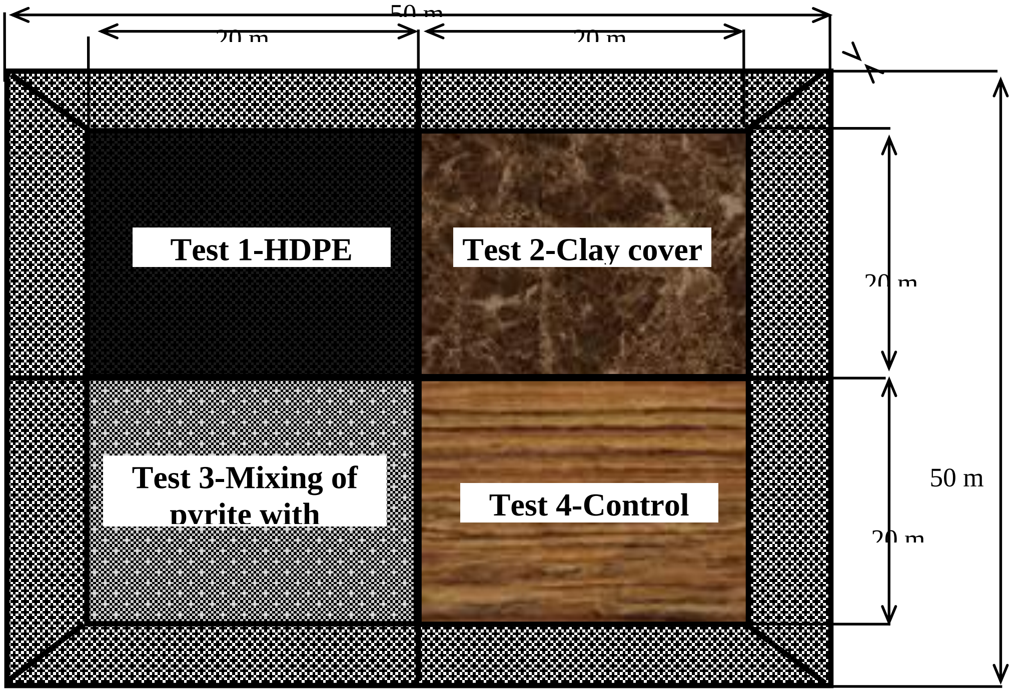

Figure 3.2. *Plan view of the study area.*

The components of each test plot from the top to the bottom are given in Table 3.4; cross sections for tests 1 and 2 are shown in Figure 3.3.

Table 3.3. Components of Lavrion test plots

Components	**Test 1**	**Test 2**	**Test 3**	**Test 4**
	Covering Kavodokanos pyrites		Alkaline addition to Bodosakis pyrites	Control area Kavodokanos pyrites
Humus layer	YES, 40 cm thick	YES, 20 cm thick	YES, 20 cm thick	YES, 20 cm thick
Protective earth layer	YES, 60 cm thick	YES, 20 cm thick	Homogeneous mixture of pyrite with 20% limestone 140 cm thick	Pyrite material 140 cm thick
Drainage layer	YES, 30 cm thick	YES, 30 cm thick		
Low permeability layer	YES, HDPE 1 mm	YES, compacted clay 60 cm thick		
Geotextile	YES	YES		
Fine gravel layer	YES, 30 cm thick	YES, 30 cm thick		
Kavodokanos pyrites	Kavodokanos pyrites placed in lysimeter 10 × 10 m^2 as a 1,5 m thick layer			

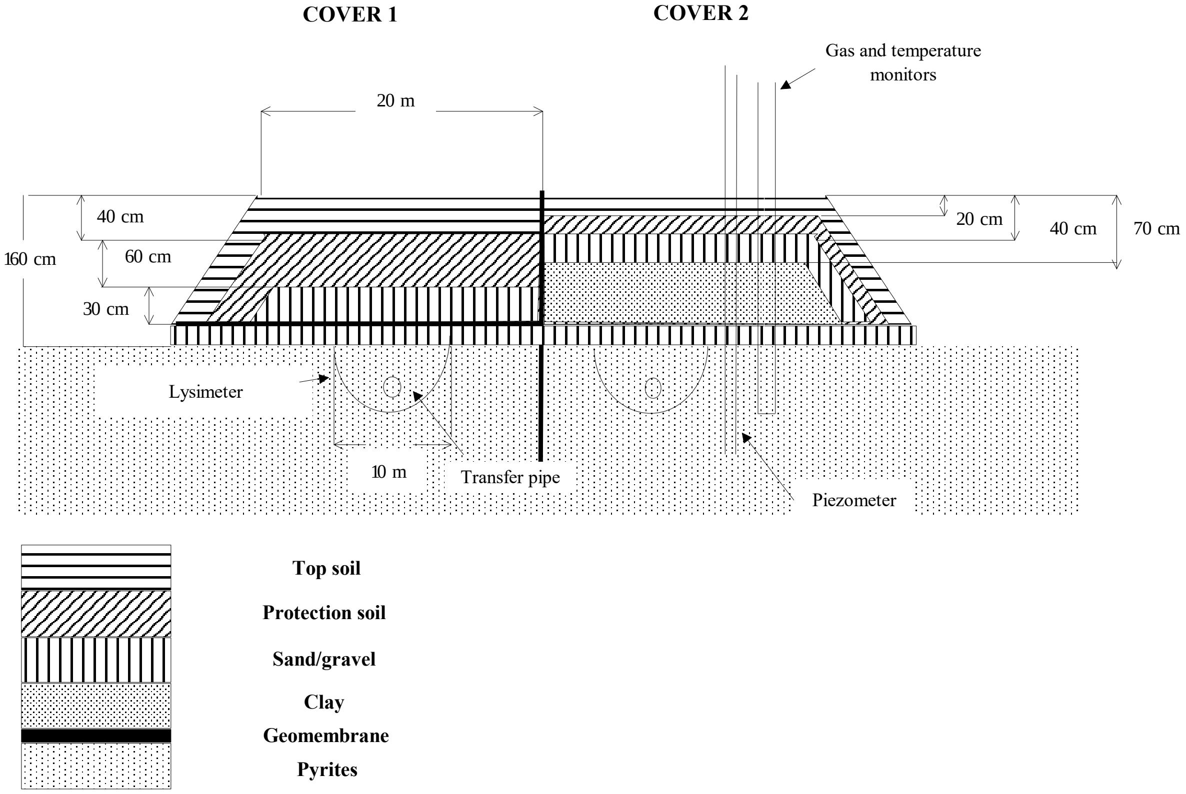

Figure 3.3. *Tests 1 and 2 involving isolation of Kavodokanos pyrites with HDPE and clay cover, respectively.*

After lysimeters installation, each test plot was constructed separately according to the configuration given in Table 3.3. Additional data regarding the characteristics of materials and methods used are described below and relevant photos are given in photographic documentation annex. It should be noted that for the construction of field plots, an effort was made to use materials and landscaping equipment available in the local market, in order to minimize the cost and stimulate the local market.

Geomembrane cover

The first layer of geomembrane cover, acting as capillary barrier, was constructed using limestone sand (Photo 12). Material had a granulometry of 81% -10+ 0.074 mm and 19% -0.074 mm and the coefficient of hydraulic conductivity was measured to $9.21\ 10^{-3}$ cm/sec. For the protection of geomembrane this was covered with a geotextile sheet (Photo 13). High Density Polyethylene (HDPE) liner, 1 mm thick manufactured by AGRU GmbH was used in the construction of the impermeable layer (Photo 14). The sheets purchased in roll width of 7 m were properly welded (Photo 15). Then a drainage layer consisting of limestone sand was formed. The function of this layer is to reduce the head of water on the HDPE layer and it would also drain the overlying protective layer.

A final 1.0m layer of protective soil was placed on top of the drainage layer. This layer is expected to accomplish the following functions:

- to store most of the infiltrating water
- to protect the underlying layers and especially the HDPE from extreme weather conditions, avoiding thus the formation of cracks, pits etc. which would enable infiltration of rainwater and oxygen in the pyrite material.

The upper layer, which is in contact with the human and biotic environment, should be constructed from a "clean" soil material, based on existing soil quality criteria. Dutch and Canadian guidelines have been used to determine the upper permitted concentrations of metal contaminants.

The quality of soils inside and around the Municipality of Lavrion exceeds highly the above mentioned guidelines. For this reason, the wider area, within 25 km from Lavrion, has been investigated to identify "clean" soil material. This task was rather difficult due to the widespread contamination all over the Lavreotiki peninsula (Demetriades *et al.* 1994). Representative results are given in Table 3.4.

Table 3.4. Chemical analysis of soil samples investigated for the construction of upper soil layer

Location, km from Lavrion	Pb (ppm)	As (ppm)	Cd (ppm)	Zn (ppm)
1. Panormos, 5 km S	*2620*	*131*	4.8	412
2. Keratea, 14 km NW	*8530*	*1368*	*39.7*	*6645*
3. Keratea, 12 km NW	320	28.5	2.8	126
4. Markopoulo, 24 km NW	*1832*	46.5	2.9	115
5. Markopoulo, 22 km NW	530	*70*	5.3	185
6. Markopoulo, 20 km NW	40	25	3.0	83

Dutch guidelines				
Target values	85	29	0.8	140
Intervention Values	530	55	12	720
Canadian guidelines				
Agricultural use	70	12	1.4	200
Residential area	140	12	10	200
Industrial area	600	12	22	720

Italics : concentrations exceeding the upper limit either in Dutch or Canadian guidelines

Selected soils

The soil No 3, originating from Keratea 12 km NW of Lavrion, has been used for the construction of the upper soil layers in all the 4 test areas. It has been also used to cover the slopes in the final landscaping of Kavodokanos heap.

Compacted clay cover

The "clean" soil No 6, originating from Markopoulo 20 km NW of Lavrion, was fine in texture and it was finally selected for the construction of the low permeability clay layer in Test 2. The major physical and geotechnical properties of this material are given in Table 3.5. The geotechnical measurements were performed in the laboratory of Edafomichaniki Ltd., Athens. Based on the American Unified Soil Classification System (AUSCS), the material is classified as sandy clay (CL) and meet the EPA requirements in terms of fines fraction (silt and clay) content, *i.e.*, higher than 20% and plasticity index, *i.e.*, higher than 10% (EPA/625/4-89/022). However, the clay material had a permeability coefficient of 3.9×10^{-6} cm/sec, higher than the one specified by EPA (*i.e.*, 10^{-7} cm/sec).

Table 3.5. Geotechnical properties of selected clay material

Parameter	Value
Grain size distribution	
Sand, -20,000 + 74 μm (%)	45
Silt, -74 + 2 μm (%)	13
Clay, -2 μm (%)	42
Atterberg limits	
Liquid limit (%)	31
Plasticity index (%)	16
Optimum moisture content (%)	16.9
Maximum dry density (t/m^3)	1.71
Permeability coefficient (cm/sec)	3.9×10^{-6}

The clay cover was formed in two lifts, each lift being 30 cm (Photos 16, 17). To check degree of compaction, a total of sixteen (16) in situ bulk density measurements were performed using the sand cone method (ASTM D 1556).

In this test, the fine gravel layer underlying the clay layer is expected to create a capillary barrier effect. Furthermore, the sand layer placed above the clay would reduce evaporation and hence cracking of the surface of the fine-grained soil.

As in the case of test 1, the construction of this plot also included the formation of a final protective soil layer with a total thickness of 40 cm.

Addition of limestone

Limestone sand used in the formation of the drainage layers (Test 1 and 2) was also used in the preparation of Bodosakis pyrites-limestone mixture. Material contained 90% $CaCO_3$ and its bulk density averaged 1.7 t/m^3, a value similar with that obtained for the Bodosakis pyrite material. Approximately 1,000 tons of the Bodosakis pyrites were excavated from the Thoricos Bay (Photos 18,19,20) and were mixed with 20 % w/w limestone. The amount of alkaline material added would sufficiently neutralise 18% of the acidity produced from the Bodosakis pyrites. The quantity of limestone applied in the field test, *i.e.*, 20% w/w was increased as compared to that used in the laboratory tests, *i.e.*, 7% w/w due to the fact that alkaline material was coarser and thus less reactive than the one used in the laboratory tests.

Given the configuration of test 3, *i.e.*, mixture of Bodosakis pyrite with limestone placed above Kavodokanos pyrite material, it is noted that the plot simulates the application of limestone addition in the upper layer of a sulphidic stockpile rather than the preparation of a homogeneous mixture, *i.e.* technique tested in the laboratory.

It is also noted that given that a) two types of sulphidic materials, *i.e.*, Bodosakis and Kavodokanos pyrite were placed in the cell and b) control area refers only to Kavodokanos material, the interpretation of any results in terms of limestone effectiveness in reducing acid generation from pyrite material may be complicated. However, it is pointed out that selection of Bodosakis pyrite as the tested material for limestone application rather than Kavodokanos sulphidic tailings was based on the fact that the first has increased acid generation potential as compared with the last thus, addition of alkaline material would result in extended precipitation of secondary products enhancing the formation of a hardpan layer.

Control Area

Control area was filled with Kavodokanos pyrites forming a layer 140cm thick and then covered with a 20cm thick top soil layer. The characteristics of Kavodokanos pyrite material used both in the control area and in the lysimeters are summarised in Table 3.6.

Table 3.6. Kavodokanos Pyrites. Summary of major geotechnical and geochemical properties of the material used in the pilot tests

Parameter	Value
Geotechnical	
Silt + Clay, < 74μm (%)	40
Permeability coefficient, field (cm/sec)	4×10^{-5}
Field density (t/m^3)	1.78
Particle density (t/m^3)	2.72
Total porosity (vol/vol)	0.434
Moisture content (vol/vol)	0.255
Acid Generation Potential	
Maximum Acid Potential, MAP (kgCaCO$_3$/t)	390±21
Neutralisation Potential, NP (kgCaCO$_3$/t)[1]	-15±7
Net Neutralisation Potential, NNP (kgCaCO$_3$/t)	405±26
Paste pH[1]	2.4±0.2

[1] Negative NP values and acidic pHs indicate a highly oxidized material

The sulphidic waste material has a very high acid generation potential, corresponding to a NNP value of -405 (±26) kg CaCO$_3$/t and it is highly oxidised as suggested by the negative NP values, -15 (±7) kg CaCO$_3$/t, and the acidic paste pH=2.4.

3.4 MONITORING RESULTS

The field tests were constructed on October1996 and they are under continuous monitoring since that date. The results presented in this section cover a period of 2 years, *i.e.* October 1996 to mid-November 1998.

3.4.1 Control Area

Quantity of percolated water

The plot produced the first drainage in January 1998, 16 months after the construction of the demo application. This long initial period was required to establish the balance between precipitation, evaporation losses and infiltration through the whole soil column above (1.6m) and inside (~0.75m) the lysimeter of the Control Area.

Precipitation (R) and evapotranspiration (ET) data, affecting the overall water balance in Lavrion area, are given in Table 3.7. As seen in this Table, Lavrion is a typically dry area; the annual precipitation amounts to 332.5 mm, whereas *potential* evapotranspiration significantly exceeds precipitation and is estimated to 812.3 mm per year based on Thornthwaite equation (Soulios 1986). The wet period, with a positive water balance between precipitation and evapotranspiration, P-ET>0, lasts only for three months, *i.e.*, December, January and February. All other months have a negative water balance, P-ET<0, with a particularly dry period between May and September, where potential evapotranspiration exceeds monthly precipitation more than 10 times.

Table 3.7. Monthly Precipitation (R) and Evapotranspiration (ET) data in Lavrion area[1]

	J	F	M	A	M	J	J	A	S	O	N	D	Annual
R, mm	54.7	56.3	30.7	22.9	7.6	4.3	2.7	4.0	4.4	43.1	37.1	64.7	**332.5**
ET[2], mm	25.3	28.5	35.7	48.9	74.3	107	124	124	102	64.0	48.9	29.4	**812.3**
P-ET	*29.4*	*27.8*	*-5.0*	*-26.0*	*-66.7*	*-103*	*-122*	*-120*	*-97.6*	*-20.9*	*-11.8*	*35.3*	

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[1] Mean monthly values based on a period of 10 years (1969-1978). Meteorological data from the Electric Power Plant in Lavrion.

[2] Potential Evapotranspiration using Thornthwaite equation (Thornthwaite, 1948); based only on mean monthly temperature.

Effective evapotranspiration during the dry period is obviously determined by the availability of water and originates from the upper layers of the soil column (evaporation zone). The depth of the evaporation zone can be estimated using as sole parameter the permeability (Schroeder *et al.* 1994, Andreottola *et al.* 1997):

$$H = 11.701 \times 1.5952^{-\log(k)} \qquad [\text{cm}]$$

where k (permeability) is expressed in cm/s. Based on this equation, the evaporation zone in Kavodokanos pyrites ($k = 4\times10^{-5}$ cm/s) extents to a depth of 91 cm.

Rough calculations indicate that no drainage is expected during the first monitoring year, in conformity with the field observations. The excess rainfall (~92 mm) of the first wet period, *i.e.*, Dec '96 to Jan '97, is not sufficient to surpass the field capacity of the waste, estimated to exceed the value of 0.33 (vol./vol.). Average moisture content of 0.29 (vol./vol.) can be only obtained with this amount of water. The ensuing dry months of year 1997 have decreased the moisture of the upper layers by evaporation, increasing again the overall water deficit inside the waste.

Drainage has been produced only after the second wet period, Dec '97 to Jan '98. The quantity of percolated water collected since January 1998 is given in Table 3.8 on a monthly basis. The maximum volume of water, *i.e.*, 733 L or 7.33L/m^2, has been collected during April 1998. The intercession of the 2nd dry period, between May and September 1998, has not nullify the production of drainage. Seasonal variations in the amount of infiltrated water are shown in Figure 3.4, together with precipitation data. The shape of the curves indicate a lag time of 4 months between the rainfall events and the collection of percolated water; additional monitoring is however required to confirm the trend.

Table 3.8. Quantity of water collected in the lysimeter of Control Area (100m^2)

Month	**Percolated water**	
	Total volume L	**Volume per surface** L/m^2 (mm)
January `98	20.0	0.20
February `98	70.0	0.70
March `98	156.7	1.57
April `98	733.3	7.33
May `98	236.7	2.37
June `98	183.3	1.83
July `98	210.0	2.10
August `98	86.1	0.86
September `98	87.2	0.87
October `98	63.3	0.63
November`98	60.0	0.60
December `98	220.0	2.20
Total	**2126.7**	**21.27**

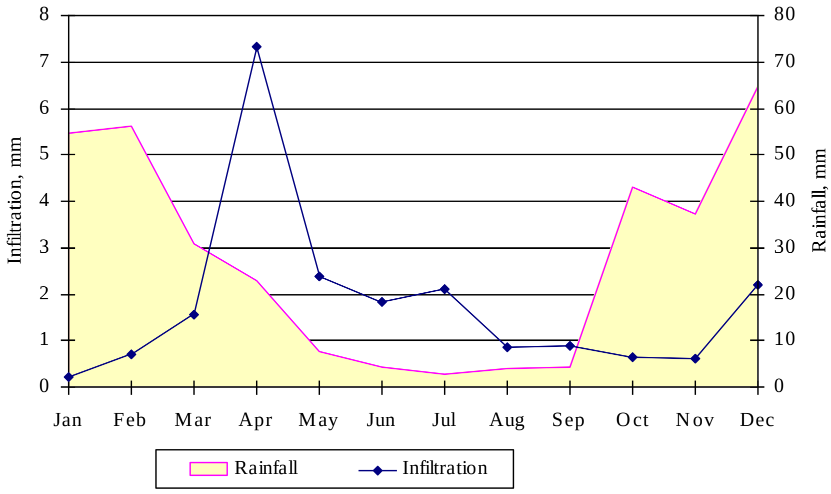

Figure 3.4. *Infiltration of water in Kavodokanos pyrites (Control Area).*

The cumulative volume of percolated water between January and December 1998 amounts to 2,127 L or 21.3 L/m^2 and corresponds to only 6.4% of the mean annual rainfall in Lavrion. The remaining 94 % has been mainly lost through evapotranspiration. Run-off losses are considered negligible given that the lysimeter is placed in the center of a leveled surface.

This high percentage of evapotranspiration is not unusual for dry areas as Lavrion. The Turc and Coutaigne empirical equations (Soulios 1986), developed for the estimation of the *annual effective* evapotranspiration, have been applied for the case of Lavrion, based on available meteo data. The calculated evapotranspiration was found to range between 90% (Coutaigne) and 96% (Turc) of the annual precipitation, close to the value observed in the field test.

From the results obtained up to now, it is estimated that the infiltration of water through the sulphidic tailings in Lavrion does not exceed 30 L/m^2 on an annual basis, due to the dry climatic conditions and the rather low permeabilities of the wastes, ranging between 2.10^{-5} (Kavodokanos pyrites) and 6.10^{-6} cm/s (Bodosakis pyrites).

Quality of percolated water

Percolated water was systematically sampled and analysed. The results are summarised in Table 3.9.

Table 3.9. Quality of drainage water in the Control Area

Parameter	Unit	Min	Max	Average
pH		0.96	1.35	1.16
Conductivity	mS/cm	26.9	31.9	30.3
Fe	mg/L	43,912	59,381	49,284
Zn	mg/L	21,607	41,217	35,937
Cd	mg/L	53.50	89.88	79.19
As	mg/L	1,410	1,680	1,541
Pb	mg/L	1.7	3.1	1.9
Mn	mg/L	675	2,646	2,096
Al	mg/L	2,602	3,263	2,985
Ca	mg/L	69.3	134.4	88.0
Mg	mg/L	485.1	926.1	564.8

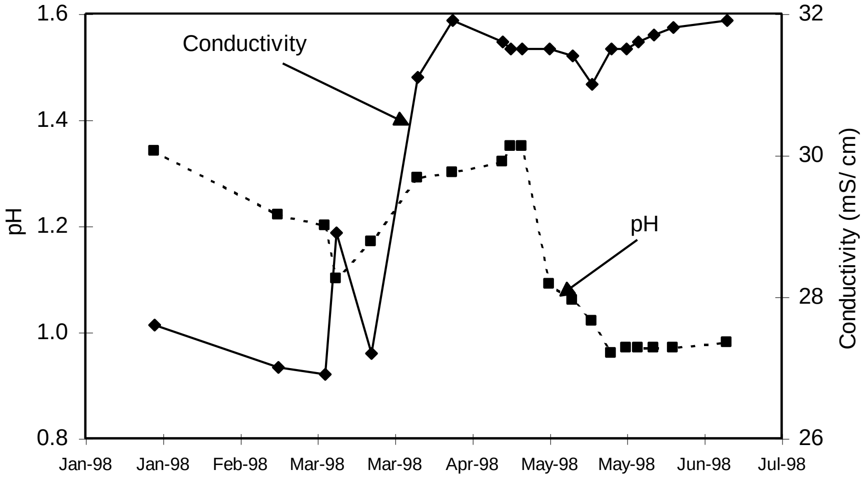

Figure 3.5. *pH and conductivity vs. time of drainage produced from the control area.*

It is seen that Kavodokanos pyrite material produced highly acidic drainage, *i.e.*, pH: 1.15±0.15 with increased conductivity values, *i.e.*, 30.3±1.9 mS/cm. Metal levels in solution were in the order of tens to thousands mg/L. The variation of pH, conductivity and metals concentration (Cd, As, Zn and Fe) vs time is shown in Figures 3.5 and 3.6.

The quality of the drainage collected in the lysimeter is indicative of the water retained in the pores of Kavodokanos pyrites. Part of this contamination is transferred downwards with the vertical movement of percolated water. Considering the annual amount of percolated water, about 20 L/m^2, it is estimated that each square meter of the pyrites contributes to the mobilisation of approximately 1000 g of Fe, 720 g of Zn, 30 g of As and 1.6 g of Cd per year, which are transferred to the underlying soils.

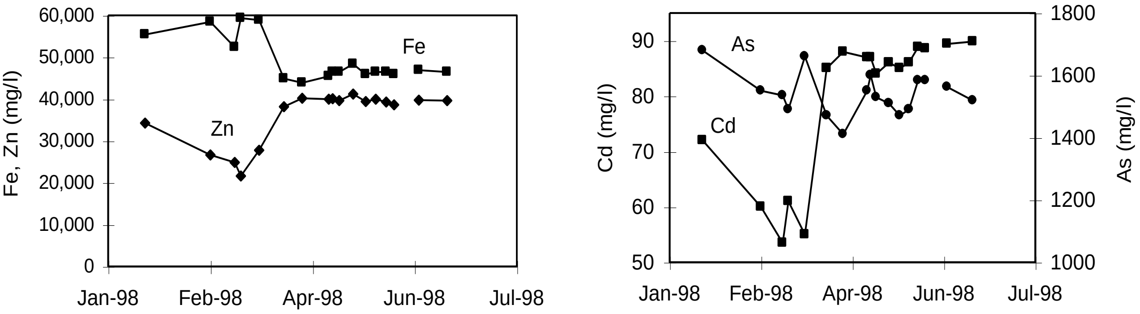

Figure 3.6. *Variation of metals concentration vs. time in the drainage produced from the control area.*

This downward movement, however, represents only part of the migration pathways for the highly acidic waters generated from the pyrites. The high evaporation potential and the resulting capillary forces contribute to transferring the contamination to the upper layers; as a consequence a simple soil cover could not isolate efficiently the waste, especially if its thickness is lower than the estimated depth of the evaporation zone. Lateral drainage is also an additional route of transferring the contamination to the surrounding soils.

3.4.2 Geomembrane cover

Covering of Kavodokanos pyrite with HDPE sheets effectively inhibited the infiltration of water into the material and no leachate was collected from this plot during the two years monitoring period.

3.4.3 Compacted clay cover

Two major concerns were related with the performance of the compacted clay cover:

a) The clay material used for the construction of the low permeability layer had a permeability coefficient of 3.9×10^{-6} cm/sec, higher than the one specified by EPA (*i.e.*, 10^{-7} cm/sec).

b) The clay layer should maintain its moisture content; loss of water could result in the formation of cracks, allowing the infiltration of rainwater and oxygen in the pyrite material.

Over the two-year monitoring period the clay cover produced drainage only during September 1998, after a rainfall event which took place on the 20th of September 1998. The drainage was detected on the 29th of September and the total amount of water was estimated to be approximately 100 L, corresponding to 1 L/m^2. No more drainage has been collected since that date.

The production of drainage is most probably related to the partial desiccation and cracking of the clay layer during the dry summer period of 1998. There is also an indication that the integrity of the clay layer has been reestablished with the first rainfalls of autumn 1998, since the drainage was completely eliminated during October and November 1998.

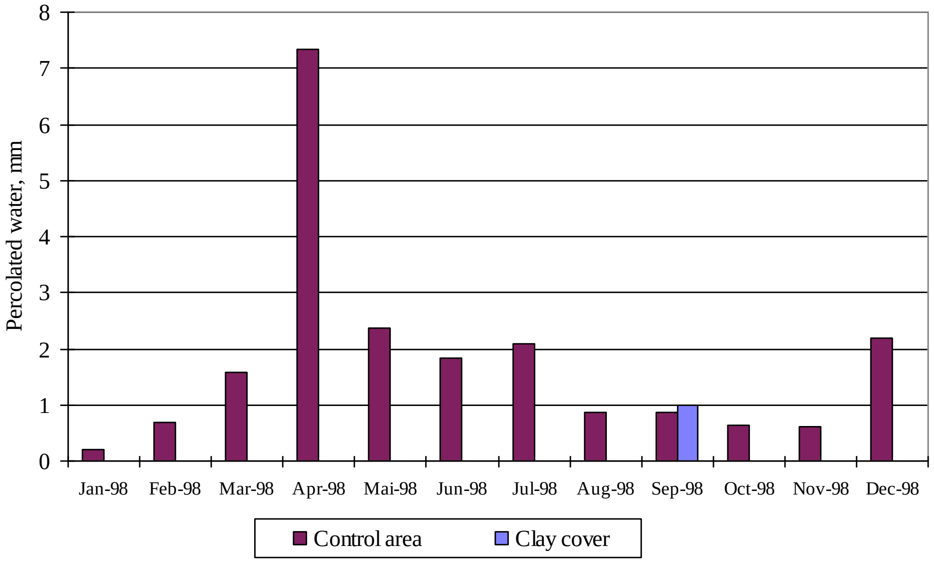

***Figure 3.7**. Water collected in the lysimeters of Control Area and Clay Cover.*

From the results obtained up to now it is deduced that the most crucial issue for the good performance of a clay cover in Lavrion area is the efficient protection of the moisture. The sandy layer of 30 cm, which was placed on the top of the clay, was not able to protect the moisture and eliminate evaporation from the underlying clay. The permeability of the sandy material used for the construction of this layer was measured to be k=9.21 10^{-3} cm/s and the corresponding depth of the evaporation zone is calculated to be 30.3 cm, *i.e.*, slightly higher compared to the actual thickness of the sandy layer, 30 cm. A better performance could be expected increasing the thickness of this layer, or using a more coarse and permeable material to act as capillary barrier above the clay.

The water collected in the lysimeter of the clay cover corresponds to approximately 5% of the drainage volume produced from the control area. This means that a 95% reduction has been achieved in the downward migration of contaminated waters, despite the accidental cracking of the clay layer. However, further monitoring is required to confirm the performance of clay layer and identify the crucial design parameters in close connection with Lavrion climatic conditions.

3.4.4 Addition of Limestone

Quantity of percolated water

This application includes the homogenous mixing of a highly sulphidic and acid generating material (Bodosakis pyrites, NNP = -800 to -1000 kg $CaCO_3$/t) with an alkaline material, *i.e.*, limestone. The role of the alkaline additive is to neutralise the acidic waters inside the pores of the mixture and promote the formation of precipitates, *i.e.*, $Fe(OH)_3$, $CaSO_4.2H_2O$, etc., resulting in cementing together the particles and forming a low permeability layer (hard pan).

The plot started to produce leachate after 17 months of operation, *i.e.* in February 1998. The volume of leachate collected from this plot is given in Table 3.10 and Figure 3.8 in comparison with the amount collected from the control area.

Table 3.10. Quantity of water collected in the lysimeter of Alkaline Additive (Hardpan) Area (100 m^2)

Month	**Alkaline Additive area**		**Control area**
	Total volume L	**Volume per surface** L/m^2	**Volume per surface** L/m^2
January `98	0.0	0.00	0.20
February `98	70.0	0.70	0.70
March `98	203.5	2.04	1.57
April `98	1010.0	10.10	7.33
May `98	1257.0	12.57	2.37
June `98	540.0	5.40	1.83
July `98	453.3	4.53	2.10
August `98	297.0	2.97	0.86
September `98	156.3	1.56	0.87
October `98	70.0	0.70	0.63
November`98	30.0	0.30	0.60
December `98	13.3	0.13	2.20
Total	**4100.0**	**41.00**	**21.27**

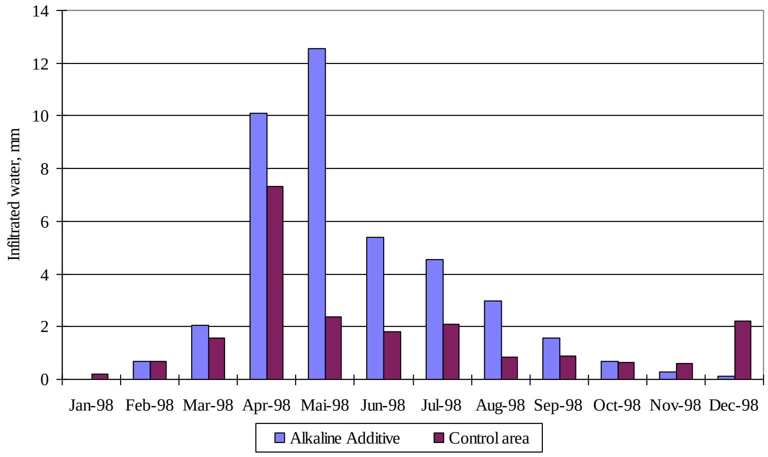

***Figure 3.8**. Leachate volume vs. month produced from the Bodosakis pyrite-limestone mixture plot-Test 3. Comparison with drainage production in the control area.*

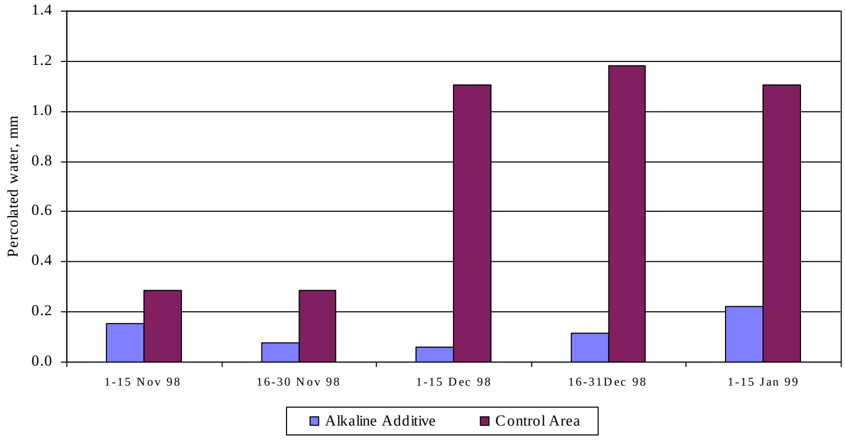

***Figure 3.9**. Bodosakis pyrite-limestone mixture. Decrease in the amount of percolated water between November 1998 and January 1999 indicating the formation of hardpan.*

The cumulative volume of leachates collected from this plot during 1998 was 41.00 L/m^2, *i.e.*, two times higher than the one reported for the control area, indicating a higher permeability of the Bodosakis pyrite - limestone mixture compared to the Kavodokanos pyrites used in the control area. It is noted that the hydraulic conductivity of Bodosakis pyrite as measured in the field was found to be very low, 6×10^{-6} cm/sec, *i.e.*, lower than the value obtained for Kavodokanos pyrite (4×10^{-5} cm/sec). The addition of limestone sand has initially increased the permeability of the material. A clear decrease in the percolation rate, indicating the formation of hardpan, has been recorded between November 98 and January 99 (Figure 3.9). Further monitoring is however required confirming this effect.

Quality of percolated water

The chemical composition of the water collected in the lysimeter of the Bodosakis pyrites-limestone area is summarised in Table 3.11.

Table 3.11. Quality of drainage water in the Bodosakis pyrites-limestone area

Parameter	Unit	Min	Max	Average
pH		1.05	1.34	1.16
Conductivity	mS/cm	26.2	36.5	33.2
Fe	mg/L	31,936	58,383	41,312
Zn	mg/L	9,681	29,441	15,478
Cd	mg/L	46.44	71.00	58.30
As	mg/L	299.6	1,680	746.3
Pb	mg/L	1.6	2.9	1.8
Mn	mg/L	1,499	7,984	5,865
Al	mg/L	1,367	2,844	1,914
Ca	mg/L	77.7	214.2	131.4
Mg	mg/L	441.0	926.1	779.1

The drainage produced from Bodosakis pyrite-20 w/w limestone plot was highly acidic, *i.e.*, pH: 1.16±0.08 and had conductivity value of 33.2±3.6 mS/cm (Figure 3.10).

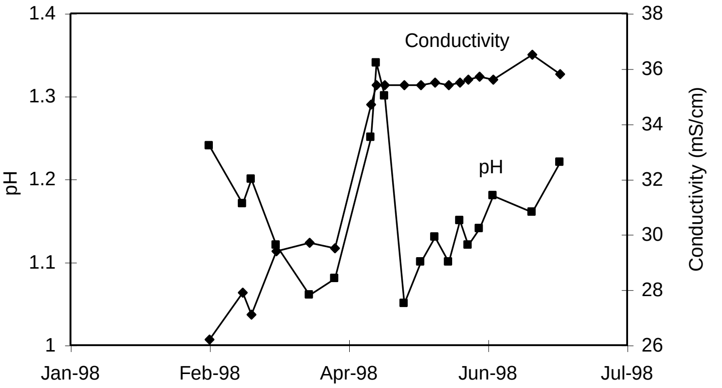

***Figure 3.10**. pH and conductivity vs. time for the leachates produced from the Bodosakis pyrite-limestone mixture-Test 3.*

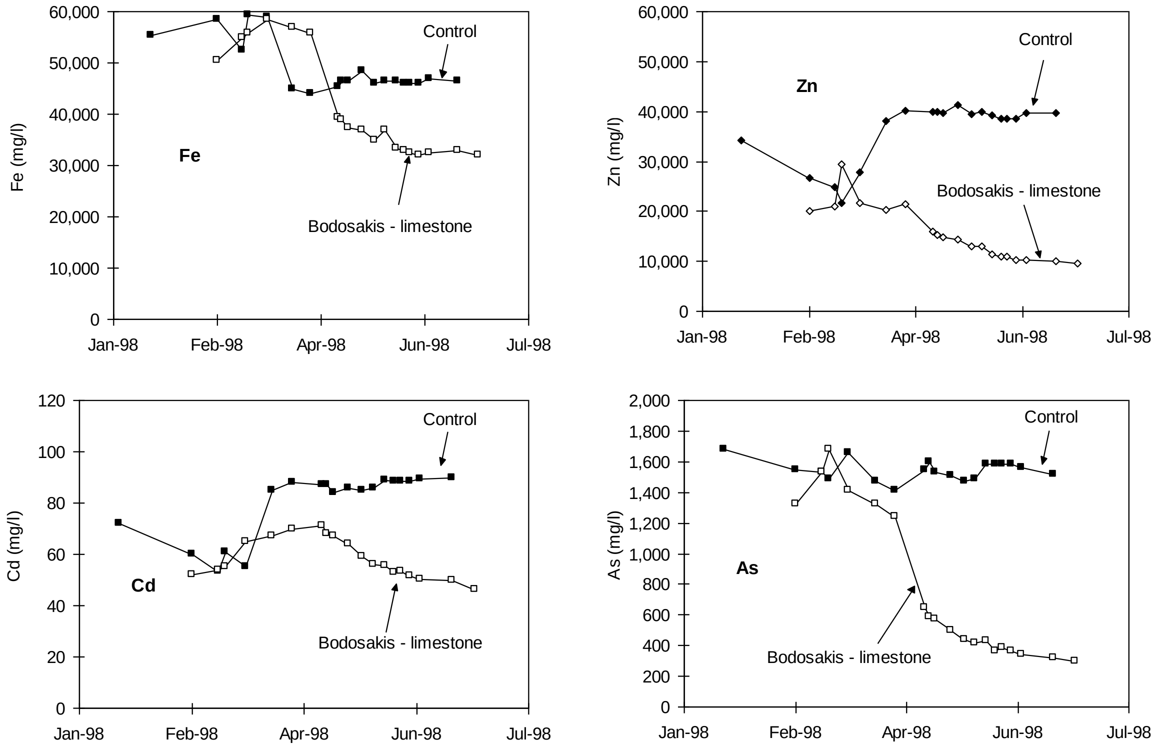

***Figure 3.11**. Metal levels in the leachate produced from limestone amended cell -test 3 as compared to the control -test 4.*

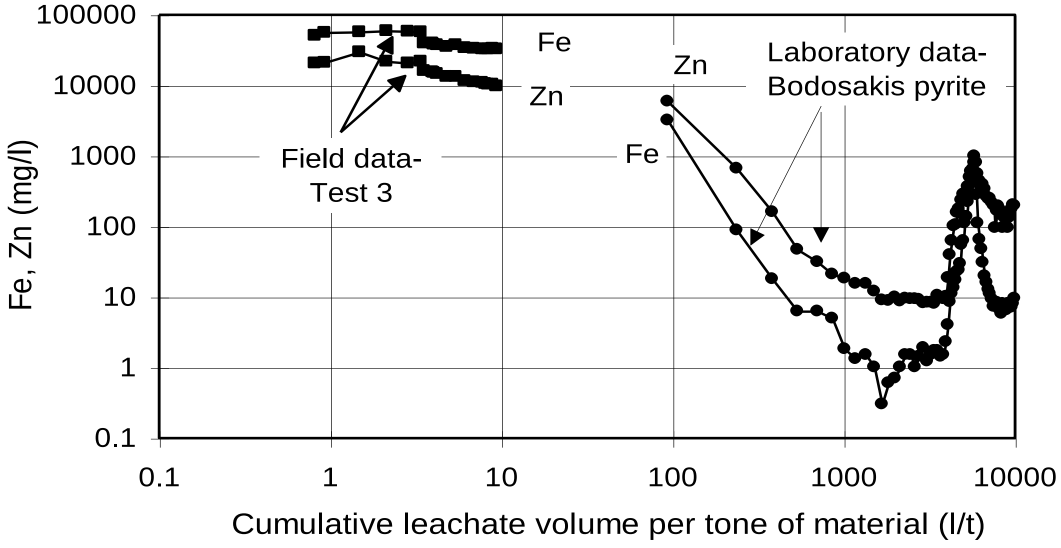

***Figure 3.11.** Fe and Zn levels in the leachate produced from limestone amended cell vs. cumulative leachate volume-Test 3. Comparison with laboratory lysimeter data on the Bodosakis pyrite material.*

It is seen that

- Drainage produced from plot 3 involving a mixture of Bodosakis pyrite with 20% w/w limestone placed above Kavodokanos pyrite had better quality as compared with that reported in the control area which was filled with Kavodokanos pyrite, *i.e.*, a material with significantly lower acid generation potential than Bodosakis. However, it is seen that dissolution of limestone contained in the upper 1.4 m thick layer could not effectively neutralise the acidity produced from the underlying 1.5 thick Kavodokanos pyrite layer and metals level in the leachates remained highly above the permissible levels for industrial effluent discharge.

- The cumulative volume of leachate per ton of material produced in the field test after two years monitoring period, *i.e.*, 10 L/t corresponds to only 10% of the leachate volume per ton of material collected in the first cycle of the laboratory lysimeter test. Based on the laboratory data, the quality of drainage is substantially improved only following the percolation of 500 L of water /t material in the lysimeter. A very long time is required in order to achieve this water/solid ratio in the field, under the conditions prevailing in Lavrion.

- The laboratory experiments were carried out applying a series of wet-dry cycles. The amount of water supplied for each wet cycle corresponds to the annual rainfall. It is obvious however that the dry cycle in the laboratory tests underestimates the evaporation phenomena observed in the field. For this reason, it is questionable whether the laboratory test simulates efficiently the long-term behavior of the material in the field. Excess water in the laboratory tests favors the neutralisation process and improves the quality of drainage. It has however a negative effect on the formation of precipitates and the final cementation of particles is inhibited. Hardpan formation is more probable in the field where evaporation favors precipitation processes.

Field data obtained during the two-year monitoring period do not indicate the formation of a hardpan layer. A very low percolation rate was recorded during November 1998, but this reduction should be confirmed with further monitoring results. Despite the low water/solid ratio which is expected to enhance the precipitation of secondary oxidation-neutralisation products, the time required under field conditions for the formation of a cemented layer is still long. It should be noted that a naturally formed hardpan layer has been observed both in Bodosakis and Kavodokanos pyrite stockpiles at Lavrion and relevant studies on their composition and effect on the inhibition of acid generation are currently performed.

3.4.5 Conclusions

Based on the results obtained from the field tests after a two years monitoring period, the following conclusions can be drawn:

- The climatic conditions encountered at Lavrion city, *i.e.*, low precipitation (332.5 mm) and pronounced dry period along with the low permeability of Kavodokanos pyrite material (4×10^{-5} cm/sec) resulted in the production of low volume of leachate, *i.e.*, 5.7% of the total annual precipitation. Drainage produced was acidic and highly contaminated in Fe, Zn, As and Cd mostly due to the washing of previous oxidation products.

- Covering of Kavodokanos pyrites with a compacted clay layer reduced the volume of leachates by 95% as compared with the control test. The production of drainage is most probably related to the desiccation and cracking of the clay layer during the dry summer period of 1998. There is an indication that the integrity of the clay layer has been reestablished with the first rainfalls of autumn 1998. Field data suggest that the most crucial issue for the good performance of a clay cover in the dry area of Lavrion is the efficient protection of clay moisture. This can be achieved by optimising the capillary brake layer on the top of the clay.

- Covering of Kavodokanos pyrites with 1 mm HDPE geomembrane effectively inhibited the infiltration of water and no leachate was produced during the two years monitoring period.

- Homogeneous mixing of Bodosakis pyrite with 20% w/w limestone has so far resulted in the increase of hydraulic conductivity of material. The cumulative volume of leachate was higher than that produced from Kavodokanos control plot and amounted to 12% of the annual precipitation. Drainage produced from this plot that involved a Bodosakis pyrite-limestone mixture placed above Kavodokanos pyrite had improved quality as compared to that reported from Kavodokanos material. However the alkalinity introduced in the water, infiltrating the limestone amended layer, was not sufficient to neutralise the acidity produced from the underlying pyrite layer and the drainage remained acidic with metals level highly above the limits for industrial effluent discharge. The expected formation of the hardpan layer was not observed during the two years monitoring period. Research is currently in progress to optimise the technique and enhances the mechanism of hardpan formation.

- Based on the results obtained up to now the geomembrane HDPE cover is the most effective technique for the prevention of acid generation from Lavrion sulphidic wastes. Compacted clay cover is a second alternative, which can have good performance if appropriately engineered. Cost data should be also considered for the final selection of technology in the case of a large-scale remediation project.

3.5. APPLICATION COST OF REHABILITATION TECHNIQUES

Based on the cost data obtained during the pilot-scale application of the rehabilitation techniques, the unit cost of alternative remedial options was calculated and a comparison was made, given in Table 3.12.

The most expensive technique is the geomembrane cover, estimated to 4,400 GRD/m^2 for an HDPE sheet of 2mm. Using a thinner sheet of 1mm, the cost is reduced to 3,100 GRD/m^2.

The cover incorporating compacted clay as the barrier layer had a cost of 2800 GRD/m^2, which is marginally lower compared to the synthetic geomembrane of 1mm.

Limestone addition at a rate of 20% may be a low cost alternative, estimated to approximately 1880 GRD/m^2. This technique can be efficient for the treatment of low-grade pyrites, when the alkalinity introduced to system is at least equivalent to the acid generation capacity of the spoils.

Table 3.12. Application cost of rehabilitation techniques under examination

Technique	Components	Unit cost (GRD/m^2)
1. Cover incorporating a HDPE geomembrane of 2mm	∗ Topsoil, 0.40 m	560
	∗ Drainage layer, (fine gravel/sand), 0.30 m thick	360
	∗ HDPE sheets, 2 mm thick	2,200
	∗ Geotextile	200
	∗ Capillary layer, (fine gravel/sand), 0.30 m thick	360
	∗ Earthworks for materials deposition	50
	∗ Overheads for construction works (18%)	670
Total		***4,400***
2. Cover incorporating a HDPE layer of 1mm	∗ Topsoil, 0.40 m	560
	∗ Drainage layer, (fine gravel/sand), 0.30 m thick	360
	∗ HDPE sheets, 1 mm thick	1,100
	∗ Geotextile	200
	∗ Capillary layer, (fine gravel/sand), 0.30 m thick	360
	∗ Earthworks for materials deposition	50
	∗ Overheads for construction works (18%)	470
Total		***3,100***
3. Cover incorporating a compacted clay layer	∗ Topsoil, 0.40 m	560
	∗ Drainage layer (fine gravel/sand), 0.30 m thick	360
	∗ Compacted clay, 0.60 m thick	720
	∗ Geotextile	200
	∗ Capillary layer, (fine gravel/sand), 0.30 m thick	360
	∗ Earthworks for materials deposition/compaction	170
	∗ Overheads for construction works (18%)	430
Total		***2,800***
4. Limestone addition 20% w/w	∗ Topsoil, 0.40 m	560
	∗ Limestone 20% w/w to a layer of 0.80m	450
	∗ Earthworks for materials deposition/mixing	580
	∗ Overheads for construction works (18%)	290
Total		***1,880***

COSTS: a) HDPE sheets: 1100 GRD/m^2 per mm thickness, including installation, b) geotextile: 200 GRD/m^2, c) gravel/sand : 1200 GRD /m^3, d) “clean soil”: 1200 GRD /m^3, e) limestone: 1920 GRD/t.

3.6 FINAL REMARKS

Two types of dry covers and the addition of limestone were tested for the rehabilitation of sulphidic tailings in Lavrion. The two covers, based on the use of HDPE geomembrane and a compacted clay layer respectively, were both found to provide an efficient barrier to the infiltration of rain water, suppressing thus the production of acidic waters and the migration of contaminants.

The major disadvantage of the HDPE cover, in addition to its relatively high cost, is the uncertainty about the long-term performance of the geomembrane sheet. This thin synthetic material can be subjected to several irreversible damages through mechanical penetration and chemical degradation processes. On the contrary the compacted clay option is based on the use of a natural material with known properties and predictable behavior. The most crucial issue for its good performance under the dry climatic conditions of Lavrion is the efficient protection of its moisture, which can be achieved by optimising the upper protective layers.

The limestone addition is a low-cost option, which can be efficient when applied at a rate stoichiometrically equivalent to the acid generation capacity of the spoils. Substoichiometric addition of limestone to high-grade pyrites has not resulted in the expected formation of hardpan during the two years monitoring period. Research is currently in progress to optimise the technique and enhances the mechanism of hardpan formation.

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SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION

LIFE Project, Contract No.: 93/GR/A/4/GR/4567

VOLUME 3

ENVIRONMENTAL CHARACTERISATION OF LAVRION SITE – DEVELOPMENT OF REMEDIATION TECHNIQUES

CHAPTER 4

CHEMICAL STABILISATION OF CONTAMINANTS

ATHENS, DECEMBER 1999

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4. CHEMICAL STABILISATION OF CONTAMINANTS

4.1. INTRODUCTION

This chapter addresses the problem of remediation of contaminated land with stabilisation techniques, aiming at converting the contaminants to low solubility, mobility and bioavailability forms. Oxidic tailings around the redundant lead-silver mines in Lavrion area were treated. Stabilisation was effected by mixing the soil with various inorganic and organic wastes or low cost materials, as phosphate fertilisers, fly ash, biological sludge, cement kiln dust, compost, saw dust, bentonite and combinations of some of those materials. Extensive research was carried out on the efficiency of phosphates. The effectiveness of stabilisation was evaluated by applying standard chemical extraction tests as well as biological tests, which involved growing of *Phaseolus vulgaris*. The laboratory test results provided the basis for the design of the field application.

4.2. STATE OF THE ART

Immobilization techniques are considered a promising and low cost alternative for the remediation of contaminated soils and wastes (Ying Ma 1993). They include two options: Solidification and stabilization methods.

Solidification

The treatment process by which the physical characteristics of a waste are altered to improve waste handling is solidification. This treatment process will also reduce the area of transfer of pollutants and / or minimise the toxicity of hazardous waste substances. In solidification processes, lime, fly ash, cement - kiln dust, or other additives are added to bind the soil into a cement - like mass and immobilize the metallic compounds. An option of solidification is vitrification. In vitrification processes the soil is formed into a glassy matrix by applying current across embedded electrodes (Peters and Shem 1992)

Stabilisation

Stabilization is the addition of materials to limit the solubility or mobility of a waste without necessarily improving the physical handling characteristics. Many chemicals were tested to immobilize heavy metals in - situ. These included standard cation exchange resins, Devoe - Holbein metal - scavenging molecules, natural materials (clays, molecular sieves, and greensand), hydrated lime, and ferrous sulphate. Most of these materials are either expensive or not very effective in removing heavy metals (Ying Ma *et al.*).

Stabilisation techniques involve mixing of the soil in-*situ* with appropriate substances and curing for some time in order for the reactions to proceed. Stabilisation is effected by a number of mechanisms, such as:

- Organic complexation, where materials with many oxygen-containing functional groups, as -COOH, -OH, immobilize metal ions (Elliot *et al.* 1986; Hargitai 1989).
- Sorption, where metals are adsorbed on the surfaces of materials as zeolites, fly ash, bentonite, peat, etc. (Benson 1980; Leppert 1990).

- Ion exchange using clays (Yong, Warkentin and Galvez, 1990).
- Increase of the soil pH by alkaline additives as lime, fly ash, sodium hydroxide, red mud etc (Bricka and Cullinane, 1988).
- Precipitation, where metals are transformed to low-solubility compounds. Common precipitation processes include hydroxide (Bricka and Cullinane 1988; Cote 1986), phosphate (Davenport and Peryea 1991; Rabinowitz 1993; Qi Ying Ma *et al.* 1993), sulphide (Scott 1979) and silicate (Conner 1990) formation.

The use of phosphates as stabilizing agent is particularly attractive for the case of soils, where the key-contaminant is Pb. This is supported by several geochemical studies, which indicate that lead phosphate minerals are very stable under a wide range of environmental conditions. A classic and comprehensive study on this issue was published by Nriagu (1974). Nriagu has concluded that lead phosphates and more particularly chloropyromorhite, $Pb_5(PO_4)_3Cl$, are the least soluble lead minerals under most natural subaqueous and aerobic conditions. The diagrams in Figure 4.1 compare the solubility and stability of pyromorphites with other geologically important lead minerals. It is seen that pyromorphite is the most stable mineral in a wide range of pH and redox conditions.

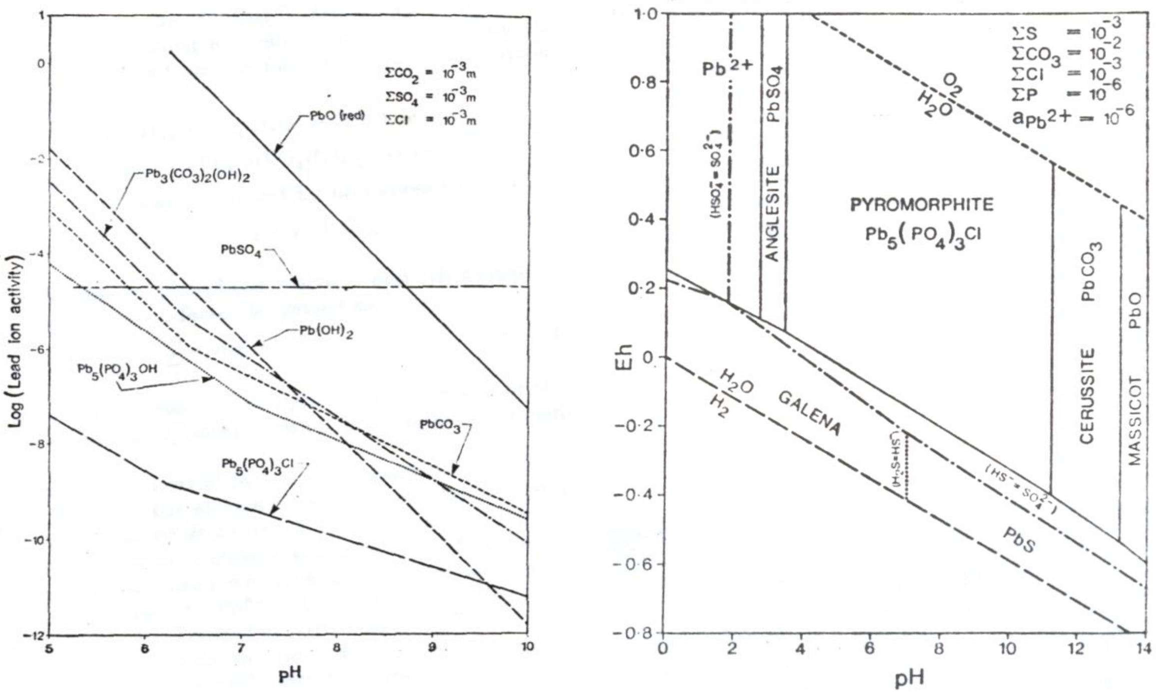

***Figure 4.1**. Solubility and stability diagrams of some common lead minerals at 25 °C (Nriagu 1974).*

Previous studies involving the use of phosphates for the stabilisation of Pb in contaminated soils are shortly described bellow.

The purpose of Ying Ma *et al.* (1993) study was to develop a technology to immobilize Pb *in situ* in contaminated soils and wastes using apatite. Hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ was reacted with aqueous Pb, resin - exchangeable Pb, and Pb - contaminated soil material. They tested also the effectiveness of natural apatite to attenuate lead. Hydroxyapatite was found to be effective in attenuating Pb in aqueous solution (from initial Pb concentrations of 5 – 500 mg/l to final Pb concentrations of 0.18 - 19.7μg/l), from resin - exchange sites, and soluble Pb from contaminated soils (from initial concentration of

2273μg/l to final lead concentration of 36μg/l). According to their results the immobilization process was rapid - about 30 min. Natural apatite was also effective in removing lead from aqueous solution. Their hypothesis was that lead was immobilized by dissolution of $Ca_{10}(PO_4)_6(OH)_2$ and precipitation of $Pb_{10}(PO_4)_6(OH)_2$. It was found that the concentration of the aqueous phosphorus is the key factor in determining the effectiveness of lead immobilization by apatite. The pH also plays a role, because it determines the solubility of the apatite. The optimal removal of aqueous lead was achieved when the pH of the solution was low enough to dissolve apatite and supply phosphorus to immobilize Pb, and high enough to keep the solubility of hydroxypyromorphite low. The final product of the lead immobilization, according to their results, was $Pb_{10}(PO_4)_6(OH)_2$.

The main idea in the work of Rabinowitz (1993) was to immobilize lead in soil by phosphate addition. The treatment of the soil consisted of mixing it with 0.03 M $Na_2HPO_4.2H_2O$ and 0.015 M NaCl solutions for 1, 3, or 7 days. After this treatment he used three different leaching reagents: 10% HNO_3, 0.5% HCl and 10% Citric acid, for testing the stabilization of Pb in the treated soil. It was found that the phosphate treatment did not have apparent effect on the nitric acid soluble fraction. The acid was able to dissolve any lead phosphate formed. The use of the other two acids, not so strong as the nitric acid, showed that the phosphate treatment, reduced the quantity of the leached lead in these acids significantly - the size of the decline averaged 49% and ranged from 33% to 76.

4.3. LABORATORY EXPERIMENTS – MATERIALS AND METHODS

4.3.1 Characterisation of soil material

The applicability of stabilisation techniques was tested on the oxidic tailings, known as "Savoura". Soil samples were taken from the surface layer (0-0.20m) near the drillhole G9, air-dried and homogenised. The most important characteristics are presented in Table 4.1.

The sampled material was found to contain 16.3 % of gravel size particles; the "soil" fraction (< 2mm) is characterised as sandy loam. It is a calcareous soil containing 26.5% of calcite equivalent and exhibiting a slightly alkaline pH. It is very poor in organic matter containing less than 0.76% of organic carbon. From the elemental analyses shown in Table 4.1, it is seen that the soil used in this experimental work is highly contaminated, mainly with Pb, Zn, Cd and As with concentrations exceeding by far existing guidelines for soils.

Table 4.1. Characterisation of the soil used in the experiments

Soil Characteristics				Elemental analyses		
Texture				*Major elements*		
	> 2 mm	(%)	16.3	Ca	(%)	12.7
Sand,	0.02-2 mm	(%)	65.8	Mg	(%)	0.9
Silt,	0.063-0.02 mm	(%)	14.5	Fe	(%)	7.0
Clay,	< 0.002 mm	(%)	3.4	Mn	(%)	0.5
pH				*Contaminants*		
pH			7.84	Pb	(%)	2.43
$CaCO_3$		mg/g	256	Zn	(%)	1.86
Organic matter				Cd	(%)	0.013
Organic carbon		(%)	0.76	As	(%)	0.30

The EPA Toxicity Characterisation Leach Procedure (TCLP) test was applied to evaluate the toxicity of the soil. The results are presented in Table 4.2 together with the regulatory limits.

Table 4.2. Toxicity of the soil following the TCLP procedure

Element	Concentration in the TCLP leachate	U.S.EPA TCLP regulatory limits
Pb	36.6	5
Zn	107	500
Cd	1.33	1
As	1	5

Mineralogical examination by X-ray diffraction revealed that the main constituents are quartz and calcite, with minor amounts of muscovite, chlorite, fluorite, albite and dolomite. Electron probe microanalysis revealed 13 minerals of Pb, Zn, Fe, Mn and Ba. Lead was found mainly in the form of carbonates ($PbCO_3$, $Pb_3(CO_3)_2(OH)_2$, $Pb_2CO_3Cl_2$) and oxides, *i.e.* Pb(OH)Cl, or associated with limonite ($FeOOH.xH_2O$).

In order to obtain a semi-quantitave estimation of the distribution of contaminants in the above mineralogical phases, the Sequential Extraction (SE) technique (Tessier *et al.* 1979) was also applied to this material and the results for Pb, Zn and Cd are presented in Table 4.3. Based on these results approximately 74% of Pb, 77% of Zn and 87% of Cd occur in the form of carbonates or as occlusions in the Fe- and Mn-oxides. A percentage of 25% for Pb, 21% for Zn and 6% for Cd is highly insoluble and remains in the residual fraction. The amount of contaminants recovered in the oxidisable fraction (*i.e.* easily soluble sulphides or ions retained in organic matter) was very limited for all three metals.

Table 4.3. Speciation of contaminants following the Sequential Extraction analysis.

	Pb	Zn	Cd
Total concentration, mg/kg	24300	18600	130
Distribution in SE fractions, %			
Exchangeable	0.0	0.0	4.2
Carbonate	23.5	21.8	28.3
Reducible (associated with Fe- and Mn- oxides)	50.4	55.2	58.7
Oxidisable (associated with organic matter or soluble sulphides)	1.3	2.2	2.8
Residual	24.8	20.8	6.0

4.3.2 Stabilizing agents

A number of inorganic and organic wastes or low cost materials were used as stabilizing agents, including phosphates, bentonite, fly ash, cement kiln dust, compost, biological sludge and saw dust. A short description of the materials is given below and their chemical composition is presented in Table 4.4.

Phosphates

Preliminary experiments, carried out with several phosphate compounds had indicated that the Ca salts are the most efficient stabilisers of Pb. Based on these results, a technical grade monohydrate-monobasic calcium phosphate, $Ca(H_2PO_4)_2 \cdot H_2O$, was selected for the laboratory tests.

Fly Ash

Two types of fly ash were used, both coming from lignite-fired power stations of Greece. The one was supplied from Kardia (Ptolemais, N. Greece) and the other one from Megalopolis (S. Greece). The chemical composition of these fly ashes are given in table 4.4. The basic difference between the two fly ashes was that the one from Kardia characterized by high CaO contend instead of the other one from Megalopolis which had high Al_2O_3 contend. In the field tests fly ash from Kardia was used.

Cement Kiln Dust

The cement kiln dust was collected from the electrostatic precipitators of the "TITAN" cement industry in Patra (Greece)

Compost

The compost originated from Athens (Liosia) municipal solid waste pilot plant, where mainly organic material from open market is being processed. The final product of the plant, before use in the laboratory, was sieved at –2mm.

Biological Sludge

The biological sludge originated from the Metamorphosis municipal wastewater treatment plant in North Athens. At this plant, the first step is the anaerobic stabilisation of the primary and the secondary sludge for 20 days at 36°C. The following step is the dewatering of the sludge by belt press, resulted in a final water contend varying from 70 to 75%.

Saw Dust

The saw dust consists of a mixture of several common commercial types of timber

Table 4.4. Chemical composition of the stabilising agents (dry basis)

	Phosphate	*Bentonite*	*Fly Ash*	*Fly Ash*	*Cement*	*Compost*	*Biol. Sludge*	*Saw Dust*
Pb (ppm)	bdl	bdl	bdl	bdl	224	263	308	bdl
Zn	28	87	80	117	238	848.5	2136	12.5
As	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cd	bdl	bdl	16	bdl	12	828	13.4	bdl
Cu	bdl	26	38	76	80	389	431	bdl
Mn	bdl	745	300	407	561	422	207	47.5
Fe (%)	0.024	2.12	2.89	5.62	0.154	2.18	1.27	0.006
Al	0.059	3.54	2.57	9.34	0.902	2.09	0.816	bdl
Ti	bdl	0.047	0.105	0.097	bdl	0.022	0.004	bdl
Ca	17.0	1.30	32.1	7.15	29.4	14.3	20.1	0.278
Mg	0.146	1.15	2.00	1.20	0.499	2.20	0.613	0.032
K	0.293	bdl	0.282	0.949	0.230	0.915	0.115	0.054
Na	0.009	1.52	0.148	0.249	0.050	0.621	0.137	0.027
SiO_2 (%)			29.00					
Al_2O_3		6.69	4.86	17.64	1.70			
Fe_2O_3		3.04	4.12	8.03	0.22			
CaO		1.82	44.91	10.01	41.16			
MgO		1.90	3.31	2.00	0.83			
K_2O		0.00	0.34	1.14	0.28			
Na_2O		2.05	0.20	0.01	0.07			
paste pH			12.6				7.9	

4.3.3 Stabilisation procedure

Stabilisation of the soil was done in pot experiments. The soil was initially sieved at 2.5 mesh in order to remove the coarse material. After this, a pre-weighed amount of soil ranging between 600-800 g was mixed with the calculated dose of stabilising agent and placed in a 1 litre pot. Phosphates were added at 12 different molar ratios of PO_4/Pb ranging between 0-2.5; this is equivalent to phosphates addition up to 3% w/w. A 1:1 PO_4/Pb molar ratio corresponds to 1% w/w PO_4 in the particular soil. All other materials were added to proportions ranging from 0 to 25% (on a dry basis). The pots were carefully watered with the appropriate amount of deionised water until a small quantity of drainage appeared in the plate under the pot. The drainage water was recycled to the pot several times every day. When the excess water was depleted due to evaporative losses, a new quantity was added and the procedure was repeated. The treatment lasted for 2 months.

4.3.4 Evaluation of stabilisation

The effect of the various additives on the stabilisation of the heavy metals in the soil was evaluated by chemical extraction tests and verified by actual biological tests. Chemical extraction tests included the following:

- Toxicity characterisation using the EPA-TCLP test
- Determination of the bioavailable-phytotoxic fraction using a combination of the following leaching tests:
    - EDTA (0.02 M Na_2-EDTA in 1N CH_3COONH_4 at pH 7.0, 10 g of soil per 100 ml, 1h agitation)
    - DTPA (0.005 M DTPA, 0.1 TAM (triethylamine), 0.01 M $CaCl_2$ at pH 7.3, 10 g of soil per 20ml, 2h agitation)
    - $NaHCO_3$ (0.5 M $NaHCO_3$ regulated at pH 8.5 with 1M NaOH, 5 g of soil per 100ml 1h agitation).

  The first two tests were used for the determination of the phytoavailable fraction of Pb, Zn and Cd, the third for that of As.

The biological tests involved plant growth using as plant indicator dwarf beans (*Phaseolus vulgaris starazagorski*). The seeds were carefully planted in the pots containing the stabilised mixure of soil. They were grown under artificial light (15 h per 24 h) in the laboratory environment; they were watered with deionised water. The plants were harvested after 22 days, when it was clear that their development was due to uptake of nutrients exclusively from the soil and not from the initial germ. The morphological parameters of the plants (root weight, leaf area, length and weight of aerial parts) were measured. Samples from the roots and leaves were collected for the determination of the metal concentrations.

4.4 RESULTS OF LABORATORY TESTWORK

4.4.1 Stabilisation using phosphates

Toxicity

As previously mentioned, the soil sample used for the development of stabilisation techniques consists from mineral processing wastes which have been deposited in the west side of Lavrion city during the first decades of the century. As a consequence it contains unusually high concentrations of metal contaminants. When subjected to the U.S. Toxicity Characterisation Leaching Procedure it is characterised as toxic, particularly for Pb which clearly exceeds the regulatory limit of 5 mg/L. The treatment with phosphates was seen to stabilise efficiently Pb (Fig. 4.2, Table 4.5). The required dose in order to reduce leachable Pb below the regulatory limit was found to be around the molar ratio PO_4/ Pb=0.6 mole/mole, which corresponds approximately to an application rate of 0.5 wt.% expressed as P_2O_5.

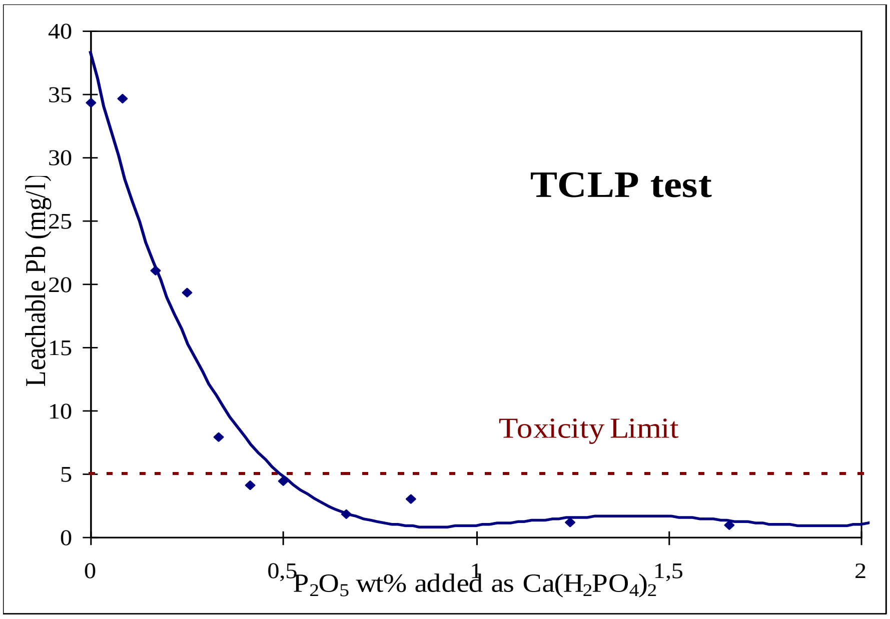

Figure 4.2. *Reduction of Pb toxicity with the phosphate treatment.*

From the results in Table 4.5 it is also seen that the treatment of soil with increasing rates of phosphates results in the stabilisation of Cd, reducing its solubility from the initial value of 1.06 mg/L down to 0.26 mg/L. On the contrary, arsenic stability was adversely affected from this treatment. Its solubility increased from the initial value of 0.19 mg/l up to 1.35 mg/l at the highest phosphate dose of 2.5 mole/mole. The mobilisation of As can be explained considering the close chemical similarity between the phosphate and arsenate ions. Traces of arsenate compounds, such as mimetite, $Pb_2(AsO_4)Cl$, have been identified during the mineralogical examination of wastes and soils in Lavrion (Boskos 1995). The above results suggest a partial substitution of arsenate ions by phosphates during this intense phosphate treatment. The corresponding release of As remains however below the toxicity limit of 5 mg/L in the whole range of phosphate doses examined in this experimental work.

Table 4.5. The effect of phosphate treatment on the toxicity of soil (U.S. TCLP)

Phosphate Dose	**Concentrations in leachate**		
PO_4/Pb, mole/mole	Pb, mg/L	Cd, mg/L	As, mg/L
0.0	*34.3*	*1.06*	0.19
0.1	*34.7*	0.53	0.35
0.2	*21.1*	0.63	0.85
0.3	*19.4*	0.39	0.99
0.4	*7.9*	0.48	1.09
0.5	4.1	0.45	1.3
0.6	4.5	0.41	1.99
0.8	2.9	0.35	1.24
1.0	3.0	0.38	1.43
1.5	1.2	0.26	1.21
2.0	1.0	0.27	1.00
2.5	1.5	0.26	1.33
Toxicity limit, mg/L	**5**	**1**	**5**

Phytoavailability

The phytoavailability of contaminants was estimated with leaching tests using chelating reagents (DTPA and EDTA) for Pb, Zn and Cd and a solution of $NaHCO_3$ for As. The pH of treated soils was also measured in order to evaluate the degree of acidification and eventual adverse effects, due to the application of the acidic phosphate salt, $Ca(H_2PO_4)_2.H_2O$. The results are presented in Table 4.6.

The application of phosphates was found to reduce efficiently the extractable fractions of Pb and Cd. On the contrary a slight increase of Zn solubility was observed increasing the phosphate dose. Finally the solubility of As in $NaHCO_3$ remained practically constant with no obvious correlation with the application rate of phosphates.

The variation of Pb, Zn and Cd leachability as a function of phosphate dose is illustrated in Fig. 4.3. For comparison reasons the extractable fraction of metals, M, was "normalized" versus the initial concentration of extractable metal, Mc, in the untreated soil. Based on the DTPA results, approximately 70% of leachable Pb and 60% of leachable Cd can be stabilized at PO_4/Pb molar ratios greater than 1.5. Following the EDTA leaching test the immobilization doesn't exceed 50% for both metals. It is also evident that stabilisation is not improved significantly when phosphates are applied at large stoichiometric excess with respect to Pb, *i.e.* PO_4/Pb > 1.0-1.5 mole/mole.

The increase of Zn solubility, up to 20%, is obviously related with the acidification of soil. Increasing the application rate of $Ca(H_2PO_4)_2$ the pH decreases from the initial value of 7.8 to 6.0 at the highest dose of 2.5 mole/mole.

Table 4.6. Effect of phosphate treatment on the pH of the soils and the phytoavailability of contaminants

Dose		Extractable metals, mg/kg of soil						
PO_4/Pb		Pb		Zn		Cd		As
mole/mole	pH	DTPA	EDTA	DTPA	EDTA	DTPA	EDTA	$NaHCO_3$
0.0	7.84	1294	5530	576	1895	9.56	28.4	21.0
0.1	7.52	1010	3670	524	2063	8.14	30.4	16.0
0.2	7.24	979	3930	560	1927	8.12	27.6	12.6
0.3	7.18	877	3050	590	1807	7.44	21.6	18.9
0.4	7.13	795	3190	557	1847	7.22	22.8	18.9
0.5	7.07	775	2710	600	1703	7.34	20.4	16.4
0.6	7.03	720	2920	599	2014	6.54	21.2	19.8
0.8	7.01	567	2560	550	1850	5.78	19.6	16.3
1.0	6.90	600	2540	621	2124	6.56	22	17.7
1.5	6.53	379	2695	643	1994	4.34	15.1	17.9
2.0	6.39	372	2646	740	2134	4.22	13.9	15.6
2.5	6.07	336	2684	615	2216	3.80	13.7	20.2

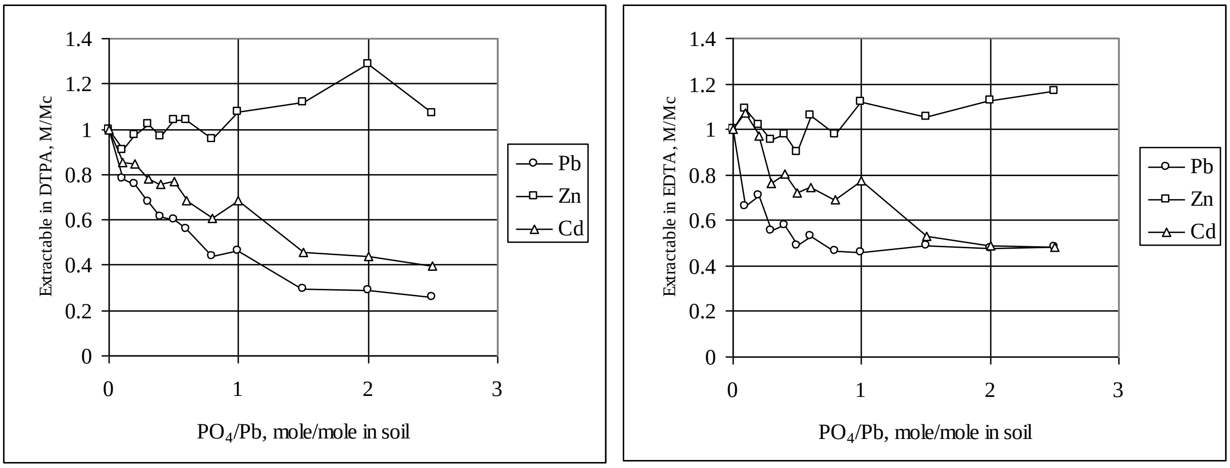

Figure 4.3. *The effect of phosphate on the leachability of metals in the DTPA and EDTA solutions. M: extractable fraction in treated soil, Mc: extractable fraction in the control experiment.*

Metal uptake in plant tissues

The concentrations of Pb, Zn, Cd and As on the leaves and roots of beans are shown in Table 4.7. The uptake of these contaminants was not significantly reduced with the treatment, up to the application rate of 2 mole/mole. Lead accumulation in the leaves varied between 100 and 250 mg/kg dry matter, Zn between 100 and 300 mg/kg, Cd between 3 and 7 and As in the range 17 to 50 mg/kg, with no obvious correlation with the dose. Very high concentrations, particularly for Zn and Cd, were measured in the leaves of the plant, grown at the soil, which was treated with the maximum phosphate dose of 2.5 mole PO_4/ mole Pb.

It must be stressed that the concentrations of metals accumulated in the leaves are very high compared to the normal range encountered in the leaves of plants (Table 4.7). Based on these experimental results, risks for grazing animals and humans through food intake are not attenuated with this treatment.

Table 4.7. Metals contents in the primary leaves and the roots of 21-day old bean seedlings

Dose	Metals contents (mg/kg dry matter)							
PO4/Pb	Pb		Zn		Cd		As	
M	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots
0.0	248	9553	240	7294	4.14	94.6	27.5	881
0.1	252	8220	173	8717	3.79	92.7	30.0	1012
0.2	101	9839	279	9943	6.34	94.6	25.6	1067
0.3	95	10284	196	9695	3.69	93.2	16.6	1320
0.4	98	10338	188	7589	3.77	135.2	22.1	880
0.5	205	5142	221	8617	4.72	74.4	49.9	1914
0.6	184	4962	227	6513	7.41	77.9	38.8	1507
0.8	99	7575	148	5563	6.31	71.7	22.8	1035
1.0	135	8203	317	4274	6.80	55.7	21.9	1376
1.5	111	7609	100	5905	9.22	57.6	23.8	1034
2.0	149	7084	175	5893	6.15	84.1	16.9	1221
2.5	245	4839	473	5163	40.3	42.9	/	365
Normal range of concentration in plant leaves, (HWLT, 1983)								
	0.1-5.0		*15-150*		*0.2-0.8*		*0.01-1*	

Plant growth

The phosphate treatment had a pronounced negative effect on plant growth mainly for the above ground parts of the plants as seen in Table 4.8. This can not be attributed to an increase of toxic metals uptake, since this effect was not observed from the analyses of plant tissues. In order to clarify the reasons for this pronounced negative effect on plants growth, selected samples of leaves were further analysed for their content in essential nutrient elements. The elements analysed were Ca, Mg, Fe, Cu and P. The results are presented in Table 4.9. The normal range of concentrations encountered in bean tissues are also shown in this table (HWLT, 1983).

The most unexpected finding was that the phosphate treatment resulted in a strong and increasing deficiency of Ca in the tissue of leaves, although the phosphates were applied in the form of calcium salt and the treated soil contained a high percentage of calcite. The analyses of leaves in the control experiment (no phosphate addition) have also shown that the plant grown in this soil take up an excess of Fe and is clearly deficient in P. The addition of phosphates has no effect on the accumulation of Fe and increase slightly the uptake of P, without however reaching the required levels.

The above results suggest that the phosphate treatment should be combined with other additives, which could counterbalance the negative effect of phosphates on plant growth.

Table 4.8. Morphological parameters and dry-matter yield of *Phaseolus vulgaris* grown on the treated soils

Dose PO4/Pb M	Root weight (DW) g	Shoot length cm	Leaf area cm^2	Leaf weight (DW) g
0.0	0.0425	31.1	113.0	0.1812
0.1	0.0753	22.2	108.0	0.1741
0.2	0.0560	19.1	78.9	0.1452
0.3	0.0740	17.9	79.5	0.1598
0.4	0.0468	19.7	87.1	0.1698
0.5	0.0632	19.6	76.9	0.1356
0.6	0.0655	16.2	50.0	0.0905
0.8	0.0767	14.6	47.7	0.0872
1.0	0.1058	12.9	46.1	0.0912
1.5	0.0573	14.2	32.5	0.0618
2.0	0.0226	16.0	40.9	0.0862
2.5	0.0233	11.7	8.25	0.0129

Table 4.9. The effect of phosphate treatment on essential nutrients

Dose PO4/Pb M	Leaf weight g	Concentration in leaves, mg/kg (DW) Ca	Mg	Fe	Mn	Cu	P
0.0	0.1812	10198	5077	1054	154.5	28.2	936
0.5	0.1356	5693	4417	1416	66.4	37.6	1446
1.0	0.0905	5263	4803	680	87.7	36.2	1779
1.5	0.0618	2909	4739	1340	98.0	39.2	2005
		Normal range in bean leaves (Jones *et al*., 1991)					
Deficiency limit (D)		10000	3000	50	50	5	3500
Toxicity limit (T)		20000	10000	300	300	30	7500

4.4.2 Stabilisation using industrial wastes and byproducts

Toxicity

In order to develop a low cost remediation technique, several industrial and municipal wastes and by-products were tested for their efficiency in stabilizing the heavy metals in Lavrion soils. Based on the international practice, the effectiveness of the stabilisation and the required dose of additive were evaluated using the EPA-TCLP test as main decision tool. This test is widely used because it has a regulatory status and provides quantitative criteria to support decision making.

The effect of additives on the toxicity of Savoura oxidic tailings is shown in Figures 4.4 and 4.5. From the 5 inorganic additives tested, best results were obtained using phosphates and fly ash from the Ptolemais plant. These additives were successful in reducing the leachability of Pb and Cd, below the regulatory limits, *i.e.* 5mg/L for Pb and 1 mg/L for Cd. Amongst the 3 organic additives, only the biological sludge was able to stabilise efficiently Pb and Cd, satisfying the regulatory criteria. The leachability of Zn was drastically reduced with the fly ash from Ptolemais and the biological sludge. Finally, the mobility of As is adversely affected by the addition of phosphates, biological sludge; and saw dust, but remains below the toxicity limit (5mg/l As) at all doses tested.

Discussion in the followings will be focused on the three materials, which were found to satisfy the TCLP criteria, *i.e.* phosphates, fly ash (Ptolemais) and biological sludge.

Phytoavailability

In Figure 4.6 the effect of the three additives on the phytoavailable fraction of Pb, Zn, Cd and As as determined by chemical extraction tests with EDTA and $NaHCO_3$ is given. Phosphate has a pronounced effect in lowering the extraction of Pb and Cd, but has essentially no effect on Zn and As; less than 1% phosphate addition reduces Pb extraction by 50% and Cd by 40%. Biological sludge and fly ash additions of 10-15% also result in a pronounced decrease in Cd and to a lesser degree, in Pb and Zn extractability. On the contrary, they increase slightly the extractability of As in $NaHCO_3$.

The effect of additives on the pH of the stabilised soil is also shown in Figure 4.7. Fly ash results in a significant increase of the soil pH because of its highly basic character. Phosphates and biological sludge result in a slight decrease of the soil pH.

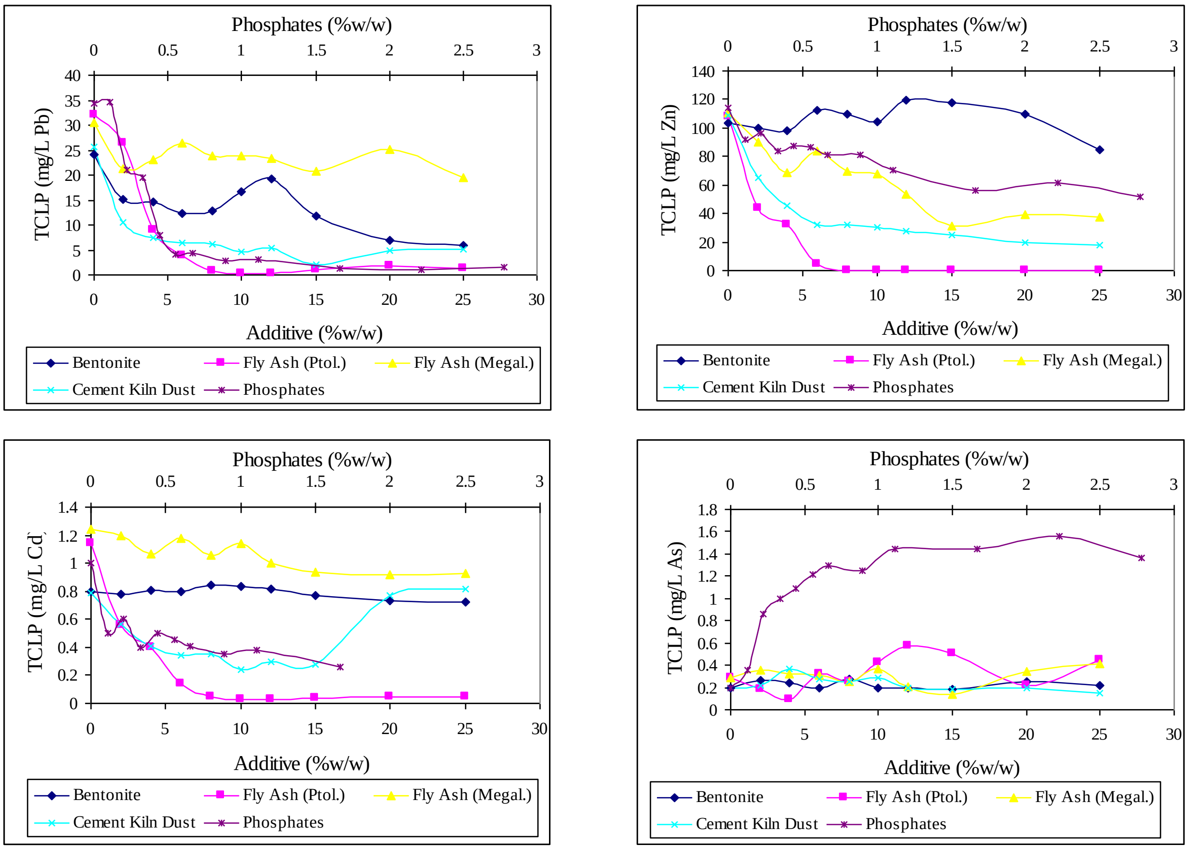

***Figure 4.4**. Effect of inorganic additives on Pb, Zn, Cd and As toxicity.*

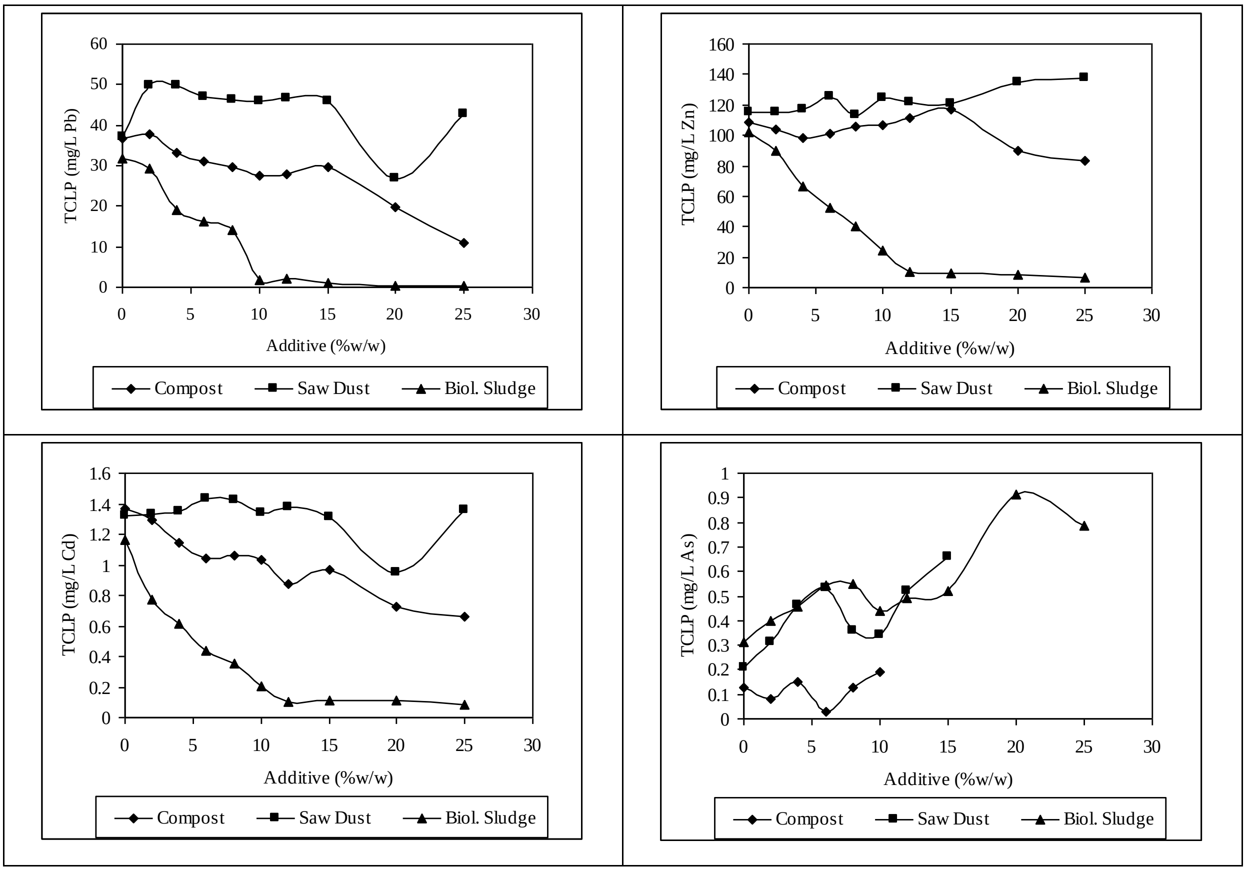

***Figure 4.5**. Effect of organic additives on Pb, Zn, Cd and As toxicity.*

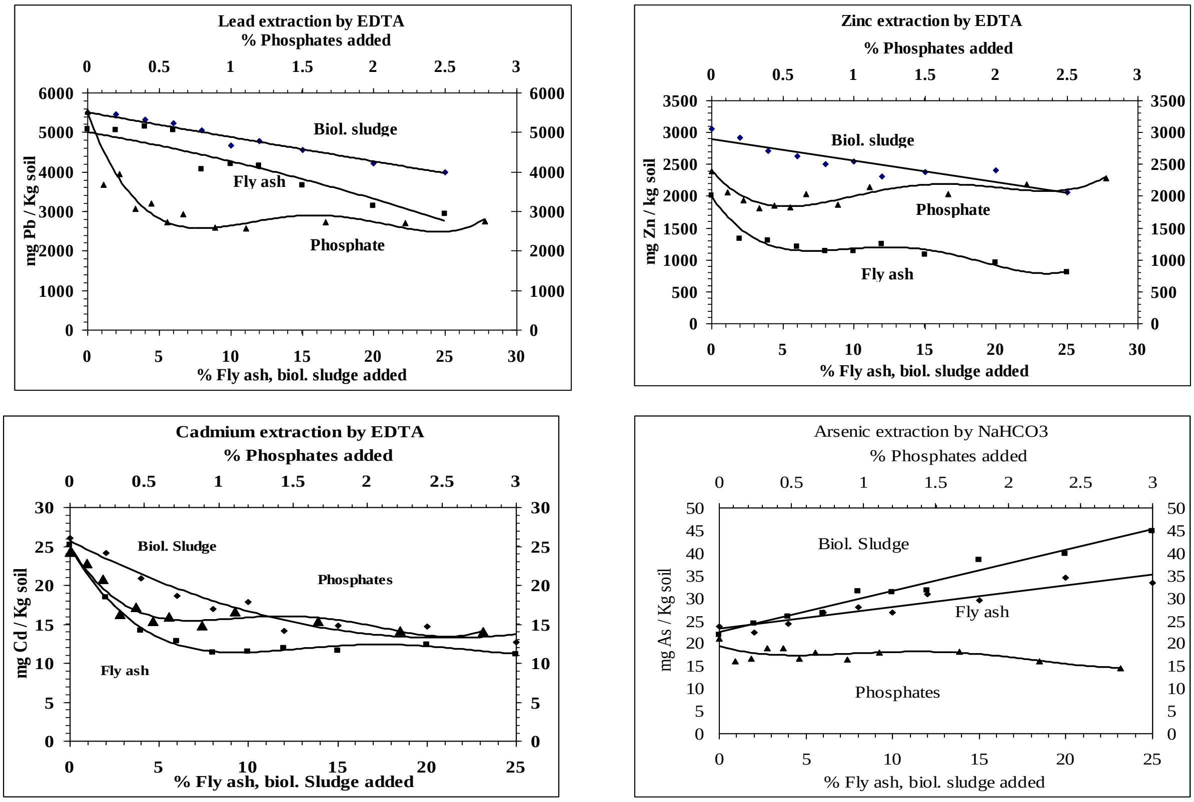

***Figure 4.6**. Evaluation of the phytoavailability with chemical extraction tests for the three successful additives.*

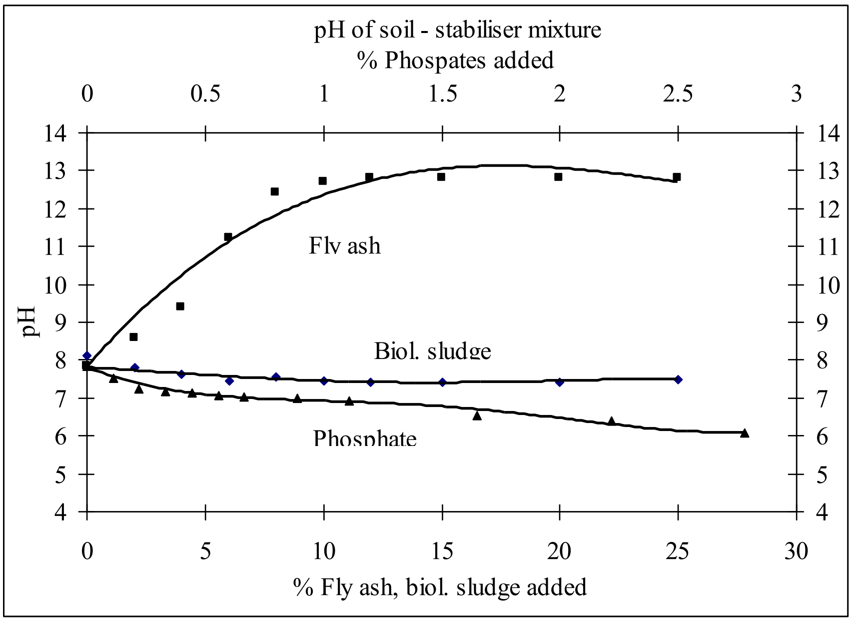

Figure 4.7. *Effect of additives on the pH of the stabilised soil.*

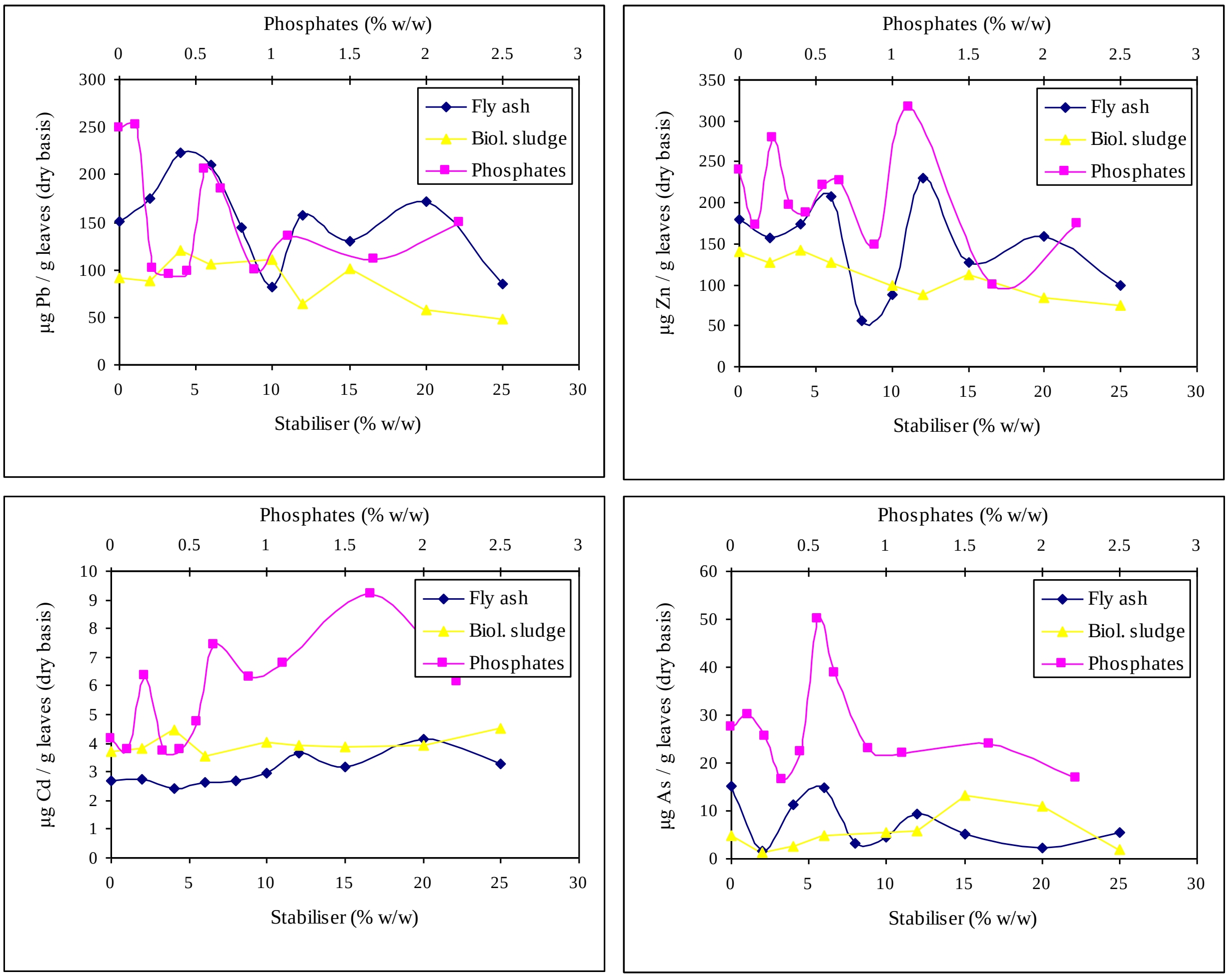

Figure 4.8. *Pb, Zn, Cd and As uptake on the leaves of beans, as a function of stabiliser addition in soil.*

In view of the results presented above, it is estimated that the stabilisation mechanisms responsible for the reduction of mobilisation of the heavy metals are:

- With phosphates: formation of insoluble lead compounds
- With fly ash: the rise of pH which results in the fixation of metal cations in the form of hydroxides; a second possible mechanism is the incorporation of metal ions in the complex silica matrix of fly ash.
- With biological sludge: organic complexation and sorption.

Metal uptake in plant tissues

The uptake of metal contaminants on the roots and leaves of beans was not reduced with the stabilisation treatment. Figure 4.8 shows the concentrations of Pb, Zn, Cd and As in the leaves of bean seedlings as a function of the stabiliser addition in soil. The data have a considerable scatter; however, the trend seems to confirm that the additives have no considerable effect on the uptake of metals.

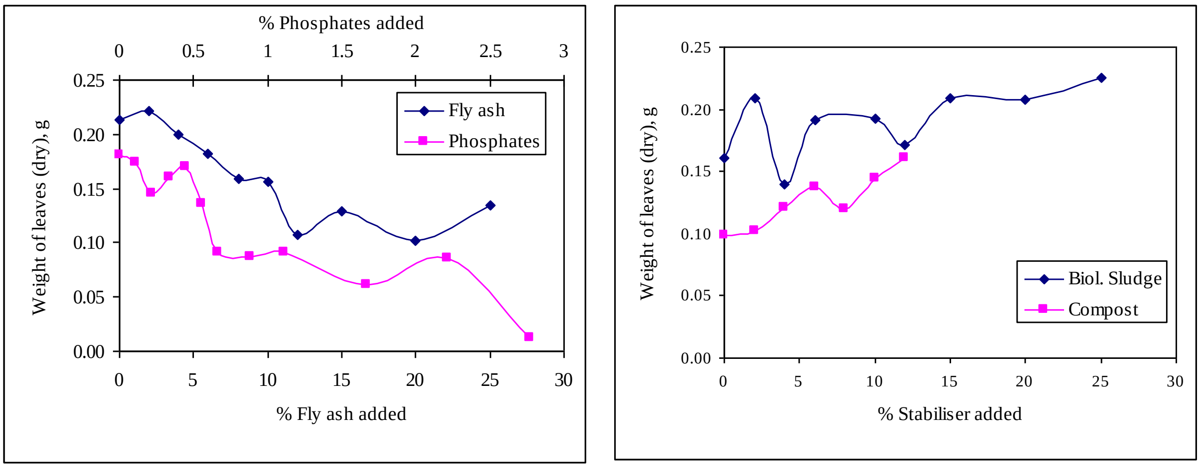

***Figure 4.9.** Effect of additives on plant growth. Weight of leaves (dry basis) vs. stabiliser dose.*

4.4.3 Conclusions

Stabilisation of the heavy metals in soil in the form of low solubility and mobility species was studied in the laboratory. The efficiency of stabilisation techniques was tested on the oxidic tailings "Savoura". This material is considered as hazardous because of the elevated concentration of heavy metals and the high bioavailable-phytotoxic fraction of heavy metals. It is also characterised as toxic according to the EPA TCLP test. Several inorganic and organic wastes and law cost materials were tested as stabilising agents. The effect of these additives was evaluated with chemical and biological tests.

Best results were obtained using *phosphates*, *fly ash* and *biological sludge*. These additives were successful in reducing the leachability of Pb and Cd, below the regulatory limits, *i.e.* 5mg/L for Pb and 1 mg/L for Cd.

Phosphate compounds are very efficient for the stabilisation of Pb; less than 1% phosphate addition reduces the TCLP leachability of Pb below the limit of 5 mg/L and its extractability in EDTA by more than 50%. The *fly ash* from Ptolemais, which is characterised by high alkalinity, was found to be very efficient for Zn and Cd. An amount of 10% was able to reduce the leachability of these elements in the TCLP solution by 98% and their extractability in EDTA by more than 50%.

Despite the reduction of heavy metals solubility, the stabilisation treatment was not able to reduce the actual uptake of toxic elements in the plant tissues, as estimated from the cultivation of *Phaseolus Vulgaris* species on the stabilised soils. The concentrations of Pb, Zn, Cd and As accumulated in the leaves remain very high compared to the normal range encountered in the leaves of plants. Risks for humans through food intake are not attenuated with this treatment, it is thus essential to avoid the cultivation of edible plants on this soil material. On the contrary, the development of a vegetative cover using non edible plant species could be highly beneficial, suppressing dusting and reducing the risks for the inhalation of airborne contaminated particles.

Concerning the effect of additives on the growth of plants it was found that both phosphates and fly ash had a negative effect while the organic rich materials, such as biological sludge and compost, showed a rather positive effect on the production of biomass.

The above results indicate that it is better to use a mixture of the successful additives in order to combine their action and obtain positive results for all the elements under investigation. Moreover a combination of inorganic and organic stabilisers is probably required to promote the development of vegetation.

4.5. FIELD TESTS

4.5.1 Introduction

Based on the results of the laboratory test work, the following rehabilitation scheme was proposed for further testing under field conditions :

- Stabilisation of the heavy metals in soils with an appropriate and cost effective mixture of the stabilisers tested. Stabilisation is expected to reduce the bioavailability of contaminants, there is no however a reliable test to predict the actual availability of contaminants in the human body.

- Development of a vegetative cover on the stabilised soil, in order to reduce risks from direct contact and air transfer of contaminated particles.

Supplementary laboratory tests were carried out using mixtures of the successful stabilisers. Phosphates and fly ash were combined with biological sludge and compost in order to reduce the leachability of all the four elements and promote the development of vegetation. The additives were mixed with the soil at various proportions to define the optimum and cost-effective dose. Based on these results five mixtures were selected for the field tests. The dose is shown in Table 4.10.

Table 4.10. Dose of stabilisers in the mixtures selected for field testing, % w/w (dry basis)

	Mixtures				
Stabiliser	**1**	**2**	**3**	**4**	**5**
Phosphate ions, PO_4^{3-}	0.44			0.44	
Fly ash		5	5		
Biological sludge			8	8	8
Compost	6	6			

The field tests were carried out in order to evaluate the efficiency and applicability of the stabilisation treatment on a larger scale. More particularly the objectives of the field tests can be summarised as follows:

- Identify the technical constraints in the application of this technique, regarding the availability of appropriate materials, equipment and personnel.
- Evaluate the efficiency under field conditions, particularly regarding the development of the vegetative cover, which is an important part of the whole rehabilitation scheme.
- Gather reliable information for the application cost of this technique, considering the alternative stabilising mixtures.

4.5.2 Stabilisation procedure in the field tests

Layout of the test area and stabilising materials

Stabilisation field tests were carried out on the carbonaceous tailings “Savoura”, at location Neraki. An area of approximately 1000m^2 was divided in six equal plots of 25m x 6m. A “dead” zone of 1m width was left between the plots. The layout of the area is shown in Figure 4.10.

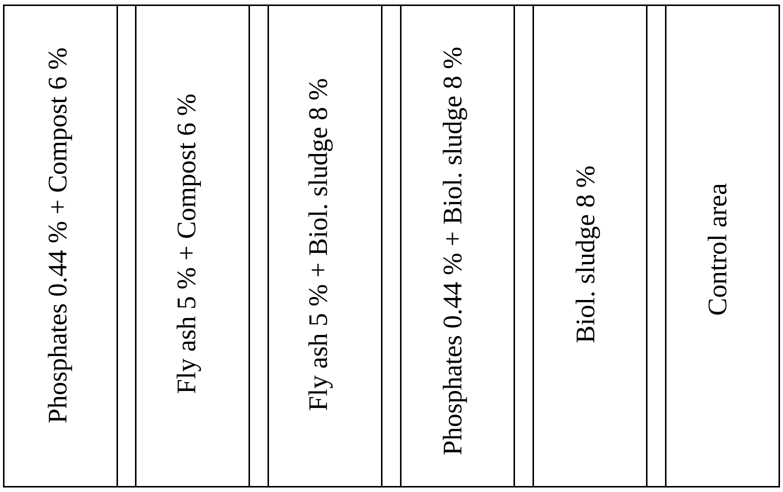

Figure 4.10. *Lay out of the stabilisation field tests.*

Stabilisation was carried out to a depth of 40 cm. So, the quantity of treated soil per plot was equivalent to 60 m^3 or 108 tons (density of soil 1.8 t/m^3). The total amount of stabilising materials used in the five plots is the following:

Phosphates

2 x 108 x 0.44% = 0.95 tons as PO_4^{3-}, corresponding to *1.5 tons* of superphosphate fertiliser (type 0-46-0).

Fly ash

2x108x5%=*11tons* of fly ash from the Public Power Station of Ptolemais, N. Greece.

Biological sludge (humidity 70%)

(3 x 108 x 8%) / 0.3 = *87 tons* of wet biological sludge from the wastewater treatment plant of Metamorphosis in North Athens.

Compost (humidity 28%)

(2 x 108 x 5%) / 0.72 = *15 tons* of wet compost from the municipal solid waste pilot plant of Liosia in Athens.

The phosphate fertilizers were delivered in plastic bags of 50kg; all other materials were transferred in bulk by trucks from the corresponding production plants. Representative pictures are shown in the photographic documentation annex.

Mixing procedure

The procedure of mixing the soil with the stabilizing materials was carried out using construction and agricultural equipment available on site. It was found that the maximum depth which can be achieved using this type of equipment is limited to 25 cm. For this reason, the mixing procedure was performed in two layers of 20cm. Due to the addition of stabilising materials, the total depth of the stabilised layer is approximately 45cm.

All earthworks were conducted between September and October 1997. The successive stages are described in detailed below:

- Preparation and cleaning of the given area
- Removal of big objects and stones (>10cm)
- Removal of the upper 20cm of soil and storage nearby
- Ploughing of the area
- Application of the stabilizing materials in quantities corresponding to the depth of 20 cm
- Mixing of the soil with the stabilizers (at least four «passages» with opposite directions)
- Transfer of the removed layer of soil in its original position and repetition of the application and mixing stages.

Representative pictures of the various stages are given in the photographic documentation volume.

Watering

Systematic watering of the area was carried out for a period of approximately 1 month in order to promote the stabilisation reactions. Initial watering was applied at a rate of approximately 50 L per square meter per day for a period of 3 days. The hydration process was repeated several times, depending on the water conditions, so that the mixture of soil and stabilizing materials remained wet. A system of artificial rain was installed in the area for the water supply. The quality of water used for irrigation satisfied drinking water standards.

Sowing

The pilot area was sown during December 1997, *i.e.* one month after the completion of the watering process. The name of the species, the amount of spores per square meter and the amount of spores per gram are given in the table 4.11.

Table 4.11

Seeds used for the development of vegetative cover on the pilot area

Type of seed	g/m^2	number of spore / g
Medicago sativa	1	520
Sanguisorba minor	10	113
Phacelia tanacetifolia	1	477
Onobtychis sativa	3	54
Lolium rigidum	1	460
Festuca ovina	1	945
Trifolium subterreaneum	2	213
Medicago lupulina	1	535
Dactylis glomerata	1	1009
Festuca rubra	1	950
Cycodon dactulon	0.5	

Several other type of seeds were also present in the mixture of spores but in small quantities (<0.15 g/m^2): *Plantago coronopus*, Anthyllis *vulleriana*, *Achillea millefolium*, *Plantago lanceulata* and *Lotus corniculatus*.

This mixture of spores includes annual and perennial species and was selected for the following reasons: the species can be developed and reproduced without special care, they can provide sufficient coverage of the surface and are considered tolerant in soils polluted with heavy metals.

NOTE: *The same scheme of sowing, i.e. species of plants and quantity of spores per sq.m., was applied to the slopes of the other test area (Kavodokanos) in a surface of more than 8000m*^{2}*, where the pyrites were covered with 20 cm of healthy soil.*

4.5.3. Evaluation of the stabilisation field tests

Toxicity tests

Soil samples were collected from the 6 plot areas after the addition of stabilizers and the watering procedure. The samples were subjected to the TCLP test to evaluate the efficiency of stabilisation, as applied under field conditions, and the results are presented in Table 4.12 and Figure 4.11. The soil material in the control area is characterized as toxic due to the high solubility of Pb and Cd. The application of stabilizing agents has reduced Pb and Cd solubility below the regulatory levels, with the exception of test area 2, where Pb exceeds slightly the limit of 5 mg/L. Zinc solubility was also reduced from the initial 100 mg/L to less than 22 mg/L. The leachability of As remained practically unaffected, varying between 0.5 and 1.1 mg/L.

Table 4.12. The effect of stabilisation in the TCLP leachability of contaminants

		Concentration in the TCLP leachate, mg/L			
Test area	**Stabilizing agents**	**Pb**	**Zn**	**Cd**	**As**
1	Phosphates + Compost	3.6	7.85	0.51	1.08
2	Fly ash + Compost	5.9	6.11	0.17	0.42
3	Fly ash + Biological Sludge	4.1	8.72	0.28	0.57
4	Phosphates + Biological sludge	3.8	6.49	0.45	0.97
5	Biological sludge	4.5	22.2	0.57	0.51
6	Control area	36.0	108.0	1.45	0.95
	TCLP limits	***5***	***500***	***1***	***5***

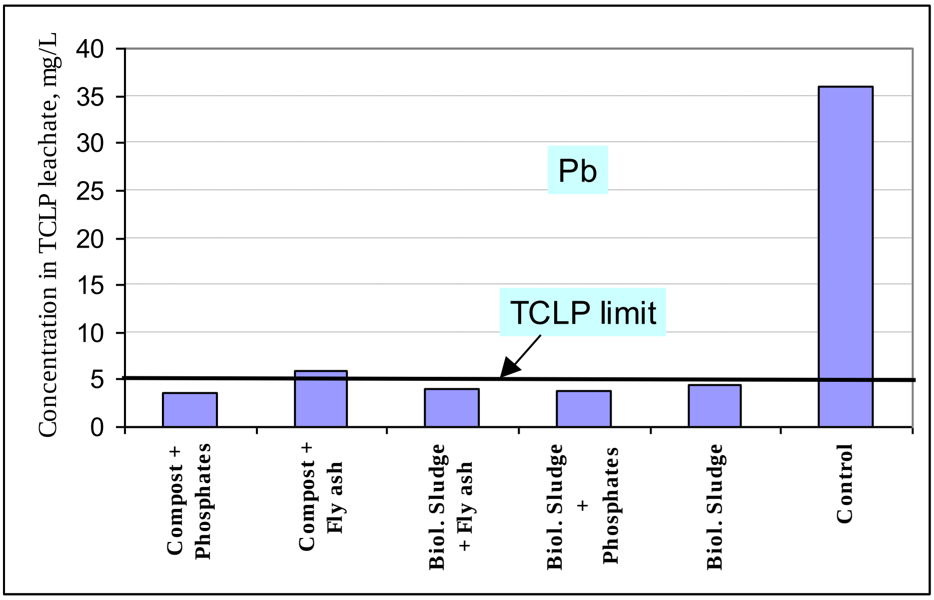

***Figure 4.11**. The effect of stabilisation in the solubility of Pb, as estimated with the TCLP tests.*

Development of vegetation

The efficiency of stabilisation was also evaluated, considering the development of vegetation. The number of plants and the production of biomass were determined in the six plot areas, just in the end of the first growing period (May 1998). The results are presented in Table 4.13. Phytomass production in the five stabilized plots, varies between 110 and 862 g/m^2, whereas in the control area it is limited to 30 g/m^2.

Representative pictures are shown in the photographic documentation annex (photos 40). The five plots, where the soil was treated with the addition of stabilizing agents, were covered with dense vegetation. Very few and poorly developed plants were grown in the control area. This difference was more pronounced during the second growing period, September 1998-May 1999 (photos 41). Plants were reproduced in the test plots 1, 2, 3, 4 and 5, which are fully covered with vegetation, while the control area 6 remained completely bare. The above results suggest that stabilisation is an indispensable pretreatment stage to support the development of vegetation and suppress air transfer of contaminated particles.

Table 4.13. The effect of stabilisation in the development of vegetation

Test area	Stabilizing agents	Number of plants No/m^2	Dry mass of plants g/m^2
1	Phosphates + Compost	1073	122
2	Fly ash + Compost	1209	112
3	Fly ash + Biological Sludge	754	158
4	Phosphates + Biological sludge	2060	550
5	Biological sludge	1827	863
6	Control area	527	29

Vegetation in Kavodokanos pyrites slopes

There were no positive results, regarding the development of plants in the slopes of Kavodokanos pyrites (photos 42). The vegetation was very poor and only very few and weakly plants were grown. This is probably due to the acidic pH of the pyrites, *i.e.* pH~2. The slopes of the heap were covered with 20cm of healthy soil. The limited depth of this layer was not sufficient to support the development of the plants and their roots have finally reached the background of acidic wastes.

4.5.4 Application cost of stabilisation techniques

Based on the cost data obtained during the pilot scale application of the stabilisation techniques, the unit cost of alternative remedial options was calculated and the results are presented in Table 4.14 and Figure 4.12.

The cost of the techniques varies between 5000 and 9700 GRD/m^2. Amongst the materials used as stabilisers, only the phosphates are a commercial product and their cost amounts to 2000 GRD/m^2. All other materials are wastes and byproducts and were delivered free of charge from the corresponding production plant. However, the transfer of stabilisers from the production plant to Lavrion was found to be the most important cost component, as shown in Figure 4.12. For instance, the cost of transferring the fly ash from Ptolemais to

Lavrion (approximately 530 km) contributes by 70 % to the total cost of the corresponding techniques.

Table 4.14. Application costs of stabilisation techniques (depth of the stabilised layer: 45 cm)

Stabilisation technique		**Components**	**Unit cost GRD/m²**
Phosphates + Compost	*	Materials	2000
	*	Transfer	1134
	*	Earthworks	456
	*	Overheads (18%)	646
	*	Vegetation	300
Total			***4686***
Fly ash + Compost	*	Materials	182
	*	Transfer	4787
	*	Earthworks	517
	*	Overheads (18%)	988
	*	Vegetation	300
Total			***6923***
Fly ash + Biological Sludge	*	Materials	182
	*	Transfer	6947
	*	Earthworks	719
	*	Overheads (18%)	1412
	*	Vegetation	300
Total			***9710***
Phosphates + Biological sludge	*	Materials	2000
	*	Transfer	3294
	*	Earthworks	658
	*	Overheads (18%)	1072
	*	Vegetation	300
Total			***7474***
Biological sludge	*	Materials	0
	*	Transfer	3240
	*	Earthworks	653
	*	Overheads (18%)	701
	*	Vegetation	300
Total			***5044***

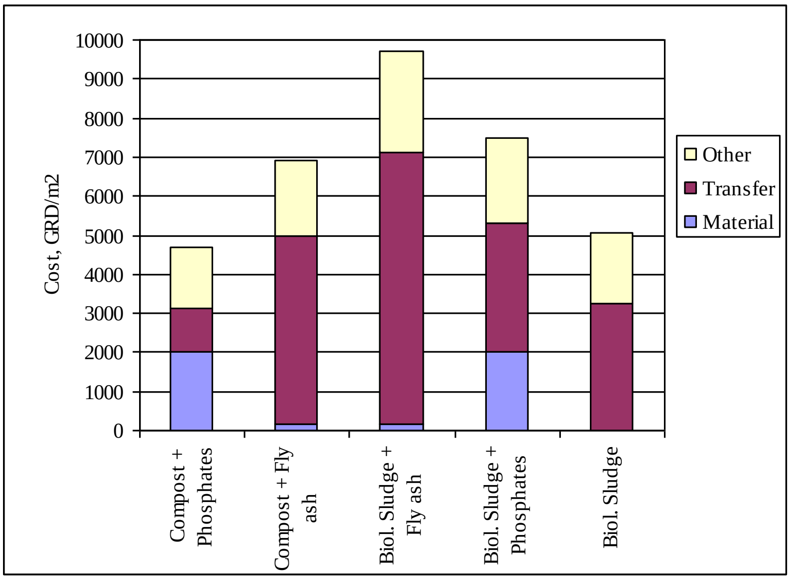

Figure 4.12. *Application costs of stabilisation techniques.*

As previously mentioned, the biological sludge used in the field tests originates from the Metamorphosis wastewater plant. In the mean time, the wastewater plant of Lavrion was put in operation. Using biological sludge from this plant would reduce substantially the cost of the corresponding rehabilitation techniques (Fig. 4.13) providing at the same time a beneficial alternative to the disposal of the sludge. Obviously, the quality of the sludge should be carefully examined to evaluate its suitability, *i.e.* levels of inorganic and/or microbiological contamination, odor, handling characteristics, etc.

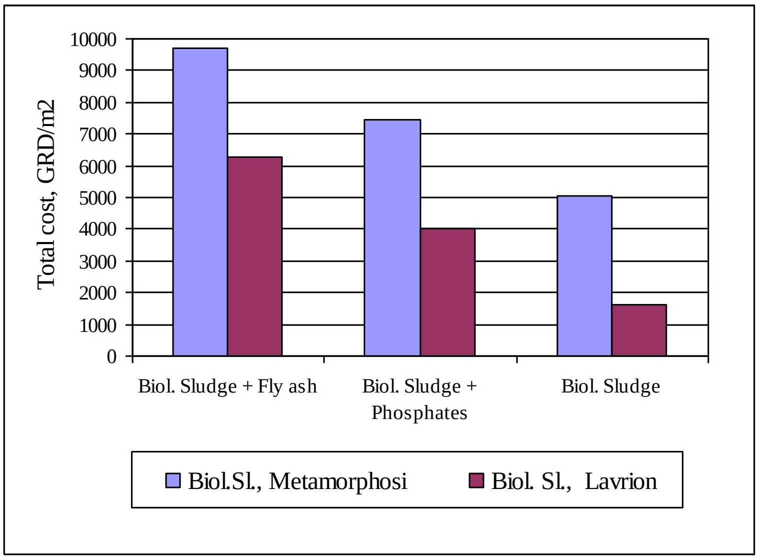

***Figure 4.13**. Comparison of costs using biological sludge from Metamorphosis and Lavrion wastewater plants.*

It is pointed out that the above cost data correspond to the stabilisation of the upper 45 cm. Increasing the depth of stabilisation will increase accordingly the treatment cost.

4.5.5 Conclusions

The applicability of stabilisation techniques was evaluated with demo-scale tests on the oxidic tailings "Savoura". Five mixtures combining phosphates, fly ash, biological sludge and compost were tested as stabilisers in the field. Stabilisation was carried out at a depth of 45 cm, using common construction and agricultural equipment.

The addition of stabilisers has reduced the solubility of Pb, Zn, and Cd by a factor ranging between 60 and 95%, and the stabilised material was characterised as non-toxic according to the TCLP test. Stabilisation was also found to be an indispensable pretreatment stage to support the development of vegetation, as a final protective cover suppressing the generation of dust.

The cost of stabilisation, as applied in Lavrion field tests, was found to range between 5000 and 9700 GRD/m^2. Considerable cost savings could be achieved using locally produced wastes and by-products.

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SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION

LIFE Project, Contract No.: 93/GR/A/4/GR/4567

VOLUME 3

ENVIRONMENTAL CHARACTERISATION OF LAVRION SITE – DEVELOPMENT OF REMEDIATION TECHNIQUES

CHAPTER 5

REMOVAL OF CONTAMINANTS

ATHENS, DECEMBER 1999

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Λευκή οπίσθια σελίδα

5. REMOVAL OF CONTAMINANTS – LEACHING TECHNIQUES

5.1 INTRODUCTION

Removal of contaminants can provide a permanent solution to the environmental problem. This category of technologies includes all the processes capable of removing the pollutants from the soil matrix with the use of physical mineral processing techniques (Trost 1993) or leaching techniques (Fristad and Weerst 1993), using the appropriate chemicals, such as mineral or organic acids, oxidation/reduction reagents or chelating agents. The application of leaching methods was investigated in the framework of this project for the removal of heavy metals from the oxidic tailings and soils of Lavrion.

Leaching techniques can be applied either in situ or by excavation and leaching on site, in heaps or using reactors. Many research efforts have been done for the development of leaching processes, but no large-scale applications have been reported. Leaching has been practised with inorganic or organic acids, such as: sulphuric (Jenkins *et al.* 1981), nitric (Royer et al, 1992) and acetic acid (Krishnamurthy 1992). For soils contaminated with lead, many studies have been carried out using the disodium or tetrasodium salt of EDTA (ethylenediaminetetraacetic acid, $C_{10}H_{16}N_2O_8$) (Elliot *et al.* 1989; Peters and Shem 1992). The use of an acidified brine (HCl-$CaCl_2$) has been proposed for a site contaminated mainly with zinc (Roche *et al.* 1994).

The successful implementation of leaching processes does not only rely on the efficient removal of metals from soils. An integrated process includes additional treatment stages, which must be optimised in order to obtain a soil remediation technique environmentally and economically acceptable:

a) Metals should be removed from the leachate and recovered in the form of a low volume solid residue, appropriate for disposal in a hazardous waste landfill area or even for recycling in the metallurgical industry.

b) In most cases the leaching solution, should be further treated, for regeneration and reuse in the leaching stage, or for final polishing in order to produce an acceptable liquid effluent for disposal in natural waters.

Most of the conventional techniques have been tested for the removal of metals and the regeneration of leaching solutions, including: precipitation with $Ca(OH)_2$, Na_2CO_3 (Jenkins *et al.* 1981) or Na_2S (Bricka *et al.* 1993); electrochemical recovery (Allen and Chen 1993) etc. The results are however contradictory regarding the efficiency and applicability of the proposed techniques, especially for the processes based on the use of organic acids and chelators.

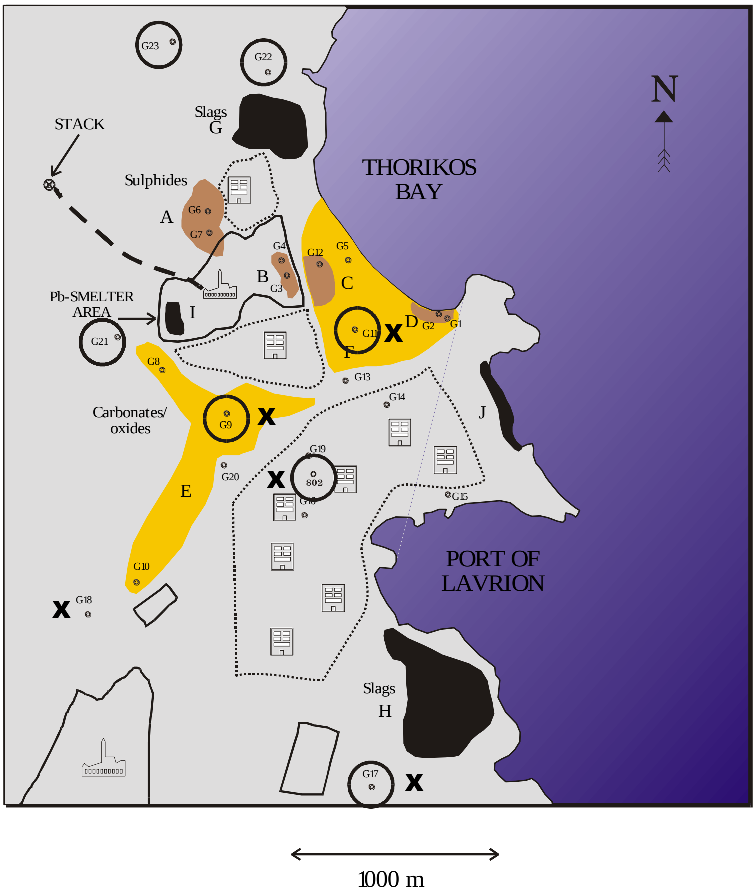
Despite the intense research activity for the evaluation of alternative reagents and techniques, a very limited number of technologies have been developed to a commercial scale. Moreover, an overall evaluation of these processes, regarding their environmental compatibility and cost effectiveness is missing. An integrated approach has been attempted in the framework of LIFE project.

5.2 EXAMINED WASTES AND SOILS

5.2.1 Description of samples

The performance of leaching techniques was evaluated on seven samples, representing the *oxidised mineral processing tailings* and the *contaminated soils* of Lavrion. The speciation of metal contaminants in these two matrices, oxidised tailings and soils, is expected to be similar. As a consequence the same leaching techniques may be appropriate for these two categories of materials. The sulphidic tailings have been excluded from this experimental work, since the occurrence of metal contaminants and their amenability to leaching techniques is expected to be very different compared to the above mentioned oxidised matrices.

The samples were selected to contain variable levels of contamination, ranging from 35 000 down to 500 mg/kg in Pb. Their location is shown in Figure 5.1. Samples G11 and G9 are characterised as "wastes", because they were collected from sites known to have been used for the deposition of milling wastes. The other samples are characterised as "soils" although a clear distinction between wastes and natural soils is not always possible. The real contours of the disposal sites are not well known. Moreover, these tailings have been often used as filling material in several construction works, spreading the contamination well beyond the boundaries of the initial deposition sites.



O : Leaching Tests, X : Mineralogical analyses

***Figure 2.1**. Location of examined wastes and soils.*

Selected properties of the samples are presented in Table 5.1, including silt/clay content (< -63μm), pH, calcite equivalent and concentrations of Ca, Pb, Zn, Cd, and As.

Table 5.1. Selected properties of the examined soils

	-63 μm wt %	Paste pH	$CaCO_3$ %	Ca %	Pb mg/kg	Zn mg/kg	As mg/kg	Cd mg/kg
Wastes								
G11	75.6	8.21	18.0	7.3	34 800	20 200	2 800	130
G9	17.9	8.65	25.6	12.7	24 300	18 600	3 000	130
Soils								
G23	42.1	8.31	31.3	11.6	32 000	15 000	1 200	100
802	15.7	8.04	26.9	10.2	12 500	10 200	1 000	80
G22	32.6	8.29	47.0	16.8	3 400	3 500	1 000	50
G17	37.6	8.25	21.0	7.3	3 200	2 400	500	40
G21	26.7	8.30	30.0	10.3	500	700	400	20

Elemental assays in soils were performed by digestion with a 1:3 mixture of nitric and hydrochloric acids and measurements of ion concentration in solution by Atomic Absorption Spectrophotometry. Paste pH was determined mixing the samples with distilled water at 1:1 solid to liquid ratio (Sobek *et al.* 1978). The calcite equivalent of the samples was determined by neutralisation of the carbonates with hydrochloric acid 0.5N and back titration of the excess acid by sodium hydroxide (Sobek *et al.* 1978).

5.2.2 Identification of Pb/Zn/As-containing phases

Mineralogical analyses were performed on five samples, G11, G9, 802, G17 and G18. (Boskos 1995). The predominant minerals, constituting the soil matrix, were identified by X-ray diffractometry and optical microscopy; electronic microscopy and microanalysis were used to identify the Pb/Zn/As-containing phases. The location of the samples is shown in Fig. 5.1 and the results are summarised in Table 5.2.

The main mineralogical phases identified in the samples are shown in Table 5.2a. The most abundant minerals were estimated to be quartz, calcite, muscovite and clinochlore. Fluorite was also found to exist in appreciable quantities in samples G11, G9 and 802.

The phases related with the occurrence of metal contaminants are shown in Table 5.2b. In order to classify and characterise these phases according to their leachability, their fate during the application of Sequential Extraction (S.E.) technique was also taken into consideration. The letters C, R, O and Rs in the second column of Table 5.2.b correspond to the Carbonate, Reducible, Oxidisable and Residual fractions following the partitioning scheme of the SE technique.

Carbonates and divalent oxides

Several carbonates ($PbCO_3$, $ZnCO_3$, $Pb_3(CO_3)_2(OH)_2$, $Pb_2CO_3Cl_2$) and a characteristic Pb oxide, Pb(OH)Cl, were identified in the microanalysis. These compounds are recovered during the second leaching stage of the SE technique (Carbonate fraction: CH_3COOH/Na, pH=5, 25°C).

Bound to Iron and Manganese Oxides

A strong association of Pb, and to a lesser extent Zn, with *iron and manganese oxides* was observed. Limonite containing up to 8.3% PbO was found in all the samples examined. It is impossible however to distinguish which is the preponderant retention mechanism: adsorption or coprecipitation. These species are released during the third leaching stage of the SE technique (Reducible fraction: $NH_2OH.HCl$, pH=3, 96°C).

Arsenates

Several Pb, Zn and Fe *arsenate* phases were also detected. It is not clear whether these minerals are dissolved and recovered in the Reducible fraction, due to the transformation of insoluble arsenates to the corresponding soluble arsenite compounds, or remain in the final Residual fraction of the SE technique.

Table 5.2a. Main mineralogical phases

		G11	G9	802	G17	G18
Quartz	SiO_2	M	M	M	M	M
Calcite	$CaCO_3$	M	M	M	M	M
Muscovite	$(K,Na)(Al,Mg,Fe)_2(Si_3AlO_{10})(OH)_2$	M	M	M	M	M
Fluorite	CaF_2	M	M	M		
Clinochlore	$(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$	M	M	M	M	M
Albite	$NaAlSi_3O_8$	M		M	M	m
Dolomite	$CaMg(CO_3)_2$	M		M		
Hydrobiotite	$K_2(Mg,Fe)_{6-4}(Fe_2,Al,Ti)_{0-2}(Si_{6-5}Al_{2-3}O_{20})O_{0-2}$	m			m	m
Talc	$Mg_3Si_4O_{10}(OH)_2$	m				
Paragonite	$Na_2Al_4(Si_3AlO_{10})(OH,F)_2$			m		
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH,F)_2$		m			
	$Ca_2(Fe^3,Al)Al(O/OH/SiO/Si_2O_7)$		m	m	m	m
Sadinine	$NaAlSi_3O_8$		m			
Hematite	Fe_2O_3			M		
Goethite	FeO(OH)	M			M	
Glaucophane					m	
Stilpnomelane					m	
Illite	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$					M
Rutile, Ilmenite,						m
Antigorite						m

M: Detected in XRD, m : Detected in Microscopy

Sulphides

The sulphur content for most of the examined materials was very low or even below the detection limit of LECO technique. Examination in Microscopy has however revealed the presence of some common sulphide minerals, such as pyrite, arsenopyrite, galena and sphalerite. Sulphide minerals are only partially dissolved during the fourth stage of the SE technique (Oxidisable fraction: H_2O_2, pH=2, 85°C).

Silicates

Association with silicates, was mainly observed for Zn and to a lesser extent for Pb and As. These compounds are thought to be highly insoluble and were attributed to the Residual fraction of the SE technique.

Combining the mineralogical data with the sequential extraction results it is possible to obtain a semi - quantitative estimation of the distribution of contaminants in the above mineralogical phases. Representative results of the Sequential Extraction Procedure, regarding the weight percent distribution of Pb in samples G11 and G9 and several representative samples of Lavrion soils (20), are also shown in the same table. From the available data it is estimated that approximately 70% of the Pb is associated with the minerals attributed to the Carbonate and Reducible fractions.

Table 5.2.b

Identification of phases containing Pb, Zn and As

	SE		**G11**	**G9**	**802**	**G17**	**G18**
Carbonates/Divalent Oxides							
Cerrussite	C	$PbCO_3$	+	+	+	+	
Hydrocerrussite	C	$Pb_3(CO_3)_2(OH)_2$		+			
Phosgenite	C	$Pb_2CO_3Cl_2$	+				
Smisthonite	C	$ZnCO_3$	+	+			
Laurionite	C	$Pb(OH)Cl$	+				
Iron and Manganese Oxides							
Limonite	R	$FeO(OH).xH_2O$	(8.3)*	(4.8)*	(6.5)*	(6.5)*	(7.0)*
	R	Pb-Fe-Mn oxides				(12)*	
	R	Pb-Mn hydrated oxides	(42)*				
	R	Pb-Fe hydrated oxides	(25)*				
	R	Pb-Zn-Mn hydrated oxides	(22)*				
	R	$PbMn(II)Mn(IV)_7O_{16}.H_2O$			+		
	R	$(Zn,Mn,Fe)(Fe,Al)_2O_4$	+	+			+
Zinkdibraunit	R	$Zn(Mn,Fe)_2O_3.2H_2O$		+	+		
Arsenates							
Mimetite	R?	$Pb_5(AsO_4)_3Cl$	+	+	+	+	
Schultenite	R?	$PbHAsO_4$			+	+	+
Beudantite	R?	$PbFe_3(AsO_4)(SO_4)(OH)_6$		+	+	+	+
Carminite	R?	$PbFe_2(AsO_4).H_2O$		+			+
Scorodite	R?	$FeAsO_4.2H_2O$		+			
Pb-jarosite	R?	$(Pb,K)Fe(SO_4,AsO_4)_2(OH)_6$				+	
Adamite	R?	Zn_2AsO_4OH		+			
Plumbogummit	R?	$PbAl_3H(PO_4)_2(OH)_6$		+			
Sulphides							
Sphalerite	O?	ZnS		+			
Galena	O?	PbS		+			
Arsenopyrite	O?	$FeAsS$	+				
Pyrite	O?	FeS_2	+	+		+	+
Silicates							
Zinksilit	Rs	$Zn_3Si_4O_{10}(OH)_2.4H_2O$		+		+	
	Rs	$Zn_4Si_2O_{17}(OH)_2.H_2O$	+	+			+
	Rs	$CaFe(II)_2Fe(III)[OH/O/Si_2O_7]$		+			
Jeffersonite	Rs	$Ca(Fe,Mg,Zn)Si_2O_6$	+				
Willemite	Rs	Zn_2SiO_4	+				
	Rs	Pb-Zn silicates			+		
	Rs	Pb-As silicates					+
	Rs	$(Fe,Mn)_2SiO_4$				+	
		Total Pb, mg/kg	34800	28200	12500	3200	4800
Pb distribution in Sequential Extraction		% Exchangeable E	0.1	/	0 - 0.1		
		Carbonate C	34.0	23.5	5 - 46		
		Reducible R	34.1	50.4	28 - 65		
		Oxidisable O	1.7	1.3	1.3 - 14		
		Residual Rs	30.1	24.8	10 - 50		
* % PbO content in the Fe-Mn Oxides							

5.2.3 Distribution of Contaminants in Particle Size Ranges

Contaminants, both organic and inorganic, are often accumulated in the fine particle fraction, *e.g.* <74μm, of the soil. Classification with regard to particle size is an option for the remediation of contaminated soils, which has already found commercial application. The fine fractions are separated from the coarse fractions using several techniques, *i.e.* tumblers, trommels, high pressure washing, sonification, hydrocyclones or vibratory screens in conjunction with sieve screens, and the contaminants are concentrated in a low volume final residue for disposal in appropriate landfills for hazardous wastes. These techniques are primarily suitable for treating pure sandy soils or sandy soils with a silt/clay content less than 10-20%. Since the small particles are for a large part concentrated in the residue a higher content is not acceptable. Typically, the soil wash systems are fixed or semi- permanent installations capable of treating 200-600 tonnes/day at costs between 50 (for pure sandy soils) and 200 USD/tone (Trost 1993; Rulkens *et al.* 1998)

In order to evaluate whether this remedial option is applicable in Lavrion soils and oxidic tailings, the distribution of contaminants as a function of soil particle size was investigated. Only two of the samples examined, *i.e.* G9 and 802, were found to have a sandy texture. Moreover, it was seen that the metal contaminants, Pb, Zn, Cd and As, were present in all size fractions of the test soils, without a clear accumulation in the fine particles < 63μm as shown in Table 5.3. Based on these results, it was concluded that the separation of fine particles is not a suitable technique for Lavrion soils and tailings.

Table 5.3. Mass distribution of contaminants in the fine particles <63μm

	Contamination Pb, mg/kg	Weight %	Pb %	Zn %	Cd %	As %
Wastes						
G11	35000	75.6	89.7	90.1	81.0	91.1
G9	28000	17.9	24.8	28.1	21.5	30.8
Soils						
G23	32000	42.1	49.0	47.7	42.7	49.5
802	12500	15.7	15.9	14.2	12.7	20.4
G18	4800	46.4	58.5	72.5	62.5	57.7
G22	3400	35.9	33.6	31.6	22.8	21.9
G17	3200	37.6	60.1	57.8	43.0	43.0
G21	500	34.4	50.8	42.6	34.4	34.4

5.3. LEACHING

5.3.1 Selection of Leaching Reagents

The selection of leaching reagents was mainly based on the chemistry of Pb, which is the key-contaminant in Lavrion soils. Lead (Pb) is a metal, which is not soluble in the common inorganic acids used in the hydrometallurgical processes, such as H_2SO_4 and HCl, due to the formation of the corresponding insoluble salts, $PbSO_4$ and $PbCl_2$. On the other hand, lead has a strong affinity for complexation and chelation (see Tables 5.4 a and b). For these reasons, the reagents evaluated during this experimental work were organic acids and chelating agents (*i.e.* acetic, citric acid, EDTA) and an acidic brine consisting of $CaCl_2$ and HCl.

The capacity of the above leaching reagents to remove metal contaminants from soils is illustrated in figures 5.2 a,b,c and d. These «solubility-pH» charts were constructed using Minteqa 2 computer program. Cerrusite, $PbCO_3$, was considered as a typical contaminant, and its solubility in water and in the presence of the above reagents is shown in these figures.

Figure 5.2a shows that, theoretically, 0.1m[1] of $PbCO_3$ is completely solubilised up to pH 12, when mixed with a solution containing a stoichiometrically equivalent amount of EDTA, 0.1m. The predominant lead specie in solution is the Pb-EDTA chelate. The reactive strength of EDTA is mainly based on its chelating capabilities. Due to the limited solubility of the corresponding tetraprotic acid, H_4-EDTA, (Table 5.4), it cannot be used in acidic solutions.

Citrate ion is a less strong chelating agent compared to EDTA (Figure 5.2b). It is able to solubilise a substoichiometric quantity of Pb, varying between 0.01m and 0.05m in the pH range 4 to 8. Based on Mintequa2 calculations, the predominant lead specie in this pH range is Pb-(citrate)$_2$ chelate. It should be mentioned however that H_3-Citrate is a highly soluble acid and leaching can be also enhanced through pH reduction.

Table 5.4

a. Formation constants of 1:1 metal chelates and complexes (Allison *et al.* 1991)

	$LogK_{ML}$			
Metal	EDTA	Citrate	Acetate	Chloride
Pb	17.88	4.34	2.87	1.60
Zn	16.44	6.10	1.57	0.43
Cd	16.28	5.30	1.93	1.98
Fe(II)	16.10	5.70	1.40	
Mn	13.87	5.28	1.40	0.61
Ca	12.40	4.73	1.18	
Mg	10.60	3.37	1.27	
Fe(III)	27.70	12.55	3.21	
Al	18.90			

b. Formation constants of lead chelates and complexes (Allison *et al.* 1991)

	$LogK_{ML}$			
	EDTA	Citrate	Acetate	Chloride
Pb-L	17.88	4.34	2.87	1.60
Pb-L_2		6.08	4.08	1.80
Pb-L_3		6.97	3.59	1.70
Pb-L_4			3.40	1.38
Pb-HL	9.68			
Pb-H_2L	6.22			

Table 5.2. Solubilities of reagents

	Molecular formula	Molecular weight	Solubility in water,
[1]Ethylene diaminetetraacetic acid (EDTA) $(HOOCCH_2)_2NCH_2CH_2N(HOOCCH_2)_2$	$C_{10}H_{16}N_2O_8$	292.24	0.1g/L at 20°C
[1]Na_2EDTA	$C_{10}H_{14}N_2O_8Na_2$	336.20	105g/L at 20°C
[1]Na_4EDTA	$C_{10}H_{12}N_2O_8Na_4$	380.17	500g/L at 20°C
[2]Citric acid, $C_3H_4(OH)(COOH)_3$	$C_6H_8O_7$	192.12	207.7g in 100g, 25°C
[2]Acetic acid, CH_3COOH	$C_2H_4O_2$	60.05	∞
[2]Calcium Chloride	$CaCl_2$	110.99	59.5g in 100g, 0°C

[1]Roger Hart, 1987, [2]Perry and Chilton, 1973

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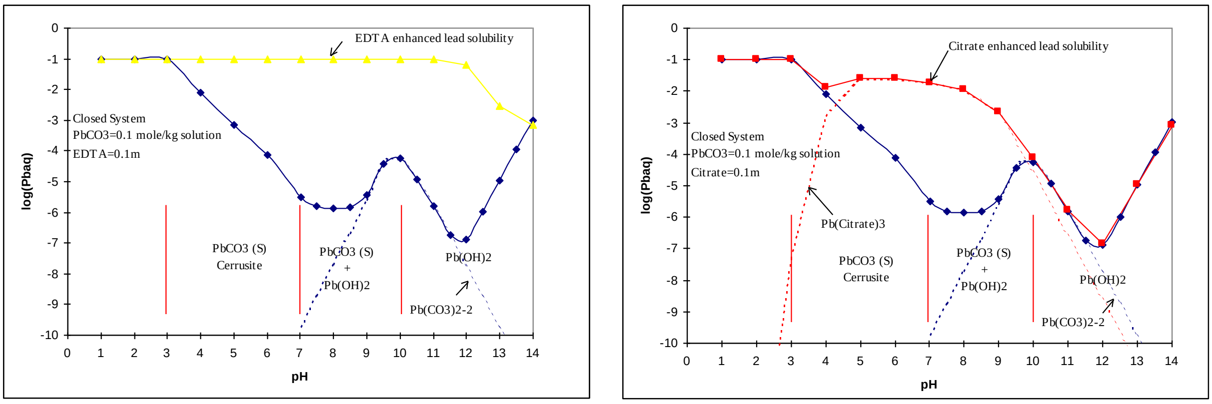
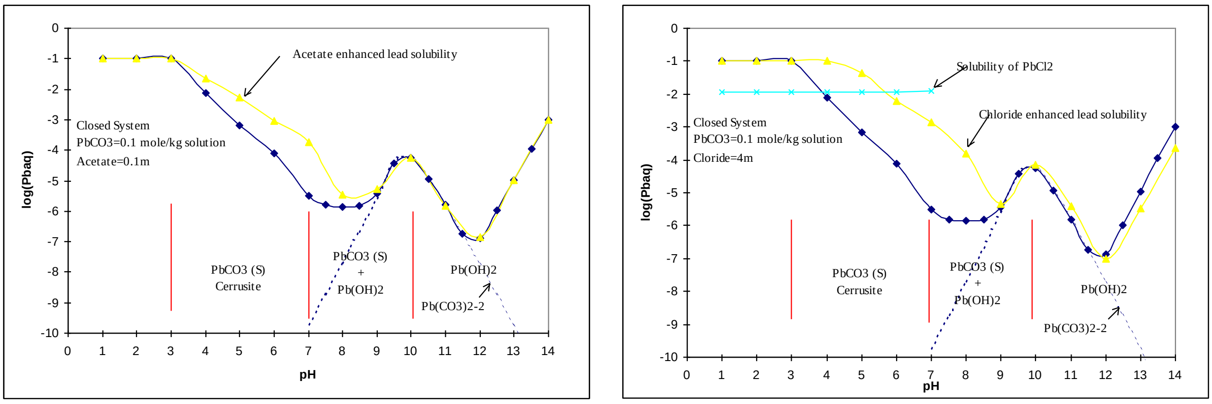
[1] All concentrations are expressed in molalities, mole/kg of solution



a) $PbCO_3$ solubility in water and 0.1 m EDTA solution

b) $PbCO_3$ solubility in water and 0.1 m Citrate solution



c) $PbCO_3$ solubility in water and 0.1 m Acetate solution

d) $PbCO_3$ solubility in water and 4 m Chloride solution

***Figure 5.2**. Enhancement of $PbCO_3$ solubility in the presence of EDTA, citrate, acetate and chloride ions. Calculated by Minteqa2, considering as predominant solids $PbCO_{3(S)}$ and $Pb(OH)_{2(S)}$.*

Figure 5.2c shows that the solubility of $PbCO_3$ is enhanced by almost one order of magnitude, when mixed with a solution containing a stoichiometrically equivalent amount of acetate ions, 0.1m, due to the formation of Pb-acetate complexes (1:1 and 1:2). The reduction of pH is however required in order to obtain the complete solubilisation of $PbCO_3$.

Figure 5.2d illustrates the effect of chloride ions, when supplied in high excess (Cl_T =4m). The solubility of $PbCO_3$ is enhanced by almost two orders of magnitude and complete dissolution can be obtained, theoretically, reducing the pH at the value of 4. The major constraint for this leaching system is that the concentration of lead in solution can not exceed the value of 0.012 m (≈2400ppm) due to the precipitation of $PbCl_2$.

5.3.2 Overview of Laboratory Testwork

The matrix in Table 5.6 summarises the experimental work, undertaken in order to evaluate the performance of these reagents on Lavrion soils and tailings and the experimental procedure which has been followed.

Table 5.6. Examined wastes and soils vs leaching reagents and experimental procedure

	OXALIC ACID	ACETIC ACID	CITRIC ACID	Na_2-EDTA	$CaCl_2$-HCl
Wastes					
G11	A	A	T/A	T/A/C	T/C
G9				T/C	
Soils					
G23			T	T	T
802			T	T	T
G22			T	T	T
G17			T	T	T
G21			T	T	T

A: Agitated reactor, T: Test tubes, C: Columns

5.3.3 Small Scale Experiments: Test Tubes

Experimental Procedure

Small-scale experiments, using test tubes of 50ml capacity, were carried out as an initial screening procedure in order to evaluate the performance of citric acid, EDTA and $CaCl_2$-HCl for the decontamination of Lavrion soils and wastes. The investigated parameters of this experimental technique included: a) level of soil contamination, b) concentration of reagents in the aqueous solution and c) solid to liquid ratio.

The experimental procedure is summarised in Table 5.7 and described in the followings:

Leaching Tests

The leaching tests were conducted in centrifuge tubes (propylene) of 50 ml capacity. Two grams of soil (dry weight) were mixed with 20 ml of the leaching solution into the centrifuge tubes. The samples were agitated on a water bath at a temperature of 25°C for 22 hours. Separation was effected by centrifugation at 3000 rpm for 15 min. The supernatant was filtrated and analyzed for the dissolved metals, whereas the solid residue was washed out 3 times with 20 ml of deionized water. Between each washing with deionized water, centrifugation was carried out and the corresponding supernatant was discarded. All leaching tests were performed in two stages. The wet washed residue of the first stage was again mixed with the leaching solution and agitated for another 22 hours at 25°C. The residue was not dried between the two leaching stages. The same procedure of solid/liquid separation and washing was applied at the end of the second leaching stage.

The samples were not dried between the two leaching stages. In order to maintain the same conditions between the first and second stages, the first leaching was also carried out on wet samples. The initial dry samples were mixed with distilled water. The water was separated by centrifugation and the tubes were weighed to determine the moisture retained by the soils. This value was used to do the required volume corrections.

The tests conducted with different soil samples were all carried out at 10% w/v pulp density. The extraction efficiency as a function of reagent concentration and pulp density was studied on the sample 802. All the experiments were carried out without adjusting the pH of the pulp.

Toxicity Evaluation

The EPA Toxicity Characteristics Leaching Procedure (TCLP) (US EPA, 1986) has been applied to characterise the residue of the two stage treatment in terms of toxicity. The test involves leaching of the residue with a buffer solution (pH=5) of sodium acetate 0.1M (64.3 ml NaOH 1N added to 933.7 ml 0.1N CH_3CH_2OOH, pH = 4.93). The solid/liquid ratio is 1/20 and the duration of the test 24 hours. Toxicity is evaluated determining the level of dissolved toxic elements in the extract; if the level of metals exceeds the specified limits, the material is characterised as toxic.

Table 5.7. Test tube experiments

	Operating Conditions
Extraction apparatus :	Test tubes 50ml
Solution volume :	20ml
Soil samlpe weight :	2 - 8 g
Temperature :	Ambient
Agitation :	Shaker bath
Duration :	2 x 22 h
Extraction stages :	Two stages with renewal of leaching solution
Solid-liquid separation:	Centrifugation
Washing :	3 stages x 20 ml water

Parameters tested

Waste and Soil Samples :	G11	G9	G23	802	G22	G17	G21

Solid to Liquid ratio, % :	10	20	30	40

Concentration of reagent, M :					
Citric acid	0.033	0.066	0.165	0.33	1.0
Na_2-EDTA	0.025	0.05	0.125	0.25	
Na_4-EDTA					1.0
Cl total= 4M, HCl	0.2	0.4	1.0	2.0	

▨ Standard conditions

Experimental Results

The Treatability of Lavrion Soils

The removal of metals obtained from the two stage treatment of Lavrion soils and wastes is presented in Table 5.8. The extraction rates were found to vary considerably for the different soil samples, without a clear trend regarding the level of contamination. The maximum removal of metals was achieved using the acidic brine, $CaCl_2$-HCl, with average extraction rates 86% for Pb, 93% for Zn and 77% for Cd. The corresponding extractions with EDTA and citric acid were 74% and 50% for Pb, 52% and 65% for Zn and 40% and 44% for Cd. Arsenic was only slightly mobilised with these leaching solutions.

The residual concentrations of contaminants after the two-stage treatment are shown in Table 5.9 in comparison with the Dutch Intervention Values for soil quality. It should be mentioned that theses concentrations were calculated based on the analyses of leachates and do not probably represent accurately the actual values. They indicate, however, that the application of leaching techniques cannot reduce the residual concentrations of these heavily contaminated samples, below these standards. Only soils of low initial contamination satisfy the intervention values for Pb, Zn and Cd following the treatment. Arsenic, which was found to be quite immobile during the leaching tests, exceeds the permissible levels in all samples.

The quality of soils was clearly improved in terms of toxicity, using the EDTA and $CaCl_2$-HCl solutions, as seen in Table 5.10. Without treatment six of the samples examined are classified as toxic due to the high levels of leachable lead. The leachability of Cd and As is below the toxicity limits for all the samples. Treatment with EDTA and $CaCl_2$-HCl was found to reduce the leachability of lead to acceptable levels, even for the highly contaminated samples, such as the waste material G11. On the contrary, four residues of the citric acid treatment were found to contain leachable species of Pb, exceeding the regulatory toxicity levels.

Table 5.8

The removal of metals from wastes and soils with variable levels of contamination

	Citric Acid, 0.33 M				**Na_2 - EDTA**, 0.25 M				**HCl-$CaCl_2$**, Cl total = 4M, H^+=2M			
	Pb	Zn	Cd	As	Pb	Zn	Cd	As	Pb	Zn	Cd	As
	Cumulative two stages extraction, (%)											
G11	53	59	53	6	65	45	44	13	83	83	88	47
G9	54	89	73	6	90	100	82	9	87	97	*100*	34
G23	48	67	47	9	71	49	37	8	61	89	65	26
802	54	63	58	18	57	45	48	18	*100*	94	*100*	70
G22	22	45	14	6	50	41	23	6	84	88	60	18
G17	65	69	40	4	98	44	27	21	90	*100*	61	49
G21	56	65	20	26	85	38	18	0	98	*100*	62	5

Table 5.9

Comparison of residual concentrations with soil quality standards

	Initial concentration (mg/kg)				Residual concentration (mg/kg)											
					Citric Acid treatment				EDTA treatment				$CaCl_2$-HCl treatment			
	Pb	Zn	Cd	As	Pb	Zn	Cd	As	Pb	Zn	Cd	As	Pb	Zn	Cd	As
Wastes																
G11	**34800**	**20200**	**130**	**2800**	**16400**	**8200**	**62**	**2600**	**12000**	**11000**	**72**	**2400**	**6000**	**3400**	15	**1500**
G9	**24300**	**18600**	**130**	**3000**	**11000**	2100	**35**	**2800**	**2400**	0	**24**	**2700**	**3100**	630	0	**1980**
Soils																
G23	**32000**	**15000**	**100**	**1200**	**16500**	**5000**	**53**	**1000**	**9300**	**7700**	**63**	**1100**	**12300**	1700	**35**	**890**
802	**12500**	**10200**	**80**	**1000**	**5700**	**3700**	**33**	**820**	**5400**	**5570**	**42**	**820**	0	570	0	**300**
G22	**3400**	**35000**	**50**	**1000**	**2600**	**1900**	**43**	**940**	**1700**	**2100**	**39**	**940**	**550**	**4300**	**20**	**830**
G17	**3200**	**2400**	**40**	**500**	**1100**	**755**	**24**	**480**	74	**1300**	**25**	**390**	330	0	**15**	**260**
G21	500	700	**20**	**400**	219	245	**16**	**290**	77	440	**16**	**400**	10	0	3.5	**370**
Dutch Intervention Values																
	530	720	12	55	530	720	12	55	530	720	12	55	530	720	12	55

Table 5.10. Characterisation of treated soils in terms of toxicity

	Initial sample				Citric acid residue				EDTA residue				HCl-CaCl$_2$ residue			
	Pb mg/l	Zn mg/l	Cd mg/l	As mg/l	Pb mg/l	Zn mg/l	Cd mg/l	As mg/l	Pb mg/l	Zn mg/l	Cd mg/l	As mg/l	Pb mg/l	Zn mg/l	Cd mg/l	As mg/l
Wastes																
G11	**146**	49.6	0,87	< 1	**14.7**	24.3	0.38	<1	**5.3**	25.6	0.17	< 1	<0.5	0.26	<0.02	1
G9	**29.7**	47.1	0.64	< 1	**15.5**	12.1	0.17	<1	3.7	12.4	0.15	< 1	2.4	0.52	0.03	2
Soils																
G23	**19.7**	20.0	0.32	< 1	**17.8**	3.7	0.12	<1	2.5	2.40	0.12	< 1	**17.8**	0.22	0.02	2
802	**12.3**	18.0	0.27	< 1	**7**	8.1	0.09	<1	0.5	2.70	0.05	< 1	<0.5	0.31	<0.02	1
G22	9	1.75	0.06	< 1	4.4	2.2	0.05	<1	1.6	0.71	0.03	< 1	0.8	0.13	0.02	2
G17	**8.4**	4.28	0.13	< 1	**5.1**	3.6	0.05	<1	0.2	0.42	0.02	< 1	<0.5	0.08	0.02	2
G21	1.6	0.52	0.04	< 1	1.7	2.6	0.03	<1	1.0	0.29	0.02	< 1	0.7	0.08	0.02	2
TCLP limits																
	5.0	500	1.0	5.0	5.0	500	1.0	5.0	5.0	500	1.0	5.0	5.0	500	1.0	5.0

The Effect of Concentration

The effect of concentration was studied on the soil sample 802 at 10% pulp density. The overall extractions of Pb, Zn and Cd as a function of concentration are also shown in Figure 5.3.

The concentrations of the citric acid, which were tested, ranged between 0.033 and 0.33M. Metals extraction was seen to double when the operating concentration was increased by 10 times. Namely, Pb extraction increased from 18.4 to 54.3 %, Zn from 30.5 to 45.4% and Cd from 22.0 to 58.5%. Increasing further the concentration to 1M has resulted in a rapid reaction with evolution of gas, probably CO_2, and part of the sample has been lost.

Four concentrations of the disodium salt Na_2-EDTA, between 0.025 and 0.25M, were tested. It should be noticed that Na_2-EDTA concentration cannot exceed the value of 0.3M, due to the limiting solubility of the disodium salt. The Na_4-EDTA was used in order to prepare a solution containing the chelant at a concentration level of 1 M. The results are presented in Fig. 5.3 together with the results obtained using the Na_2-EDTA reagent.

The maximum extraction of metals, *i.e.* 57% for Pb, 45% for Zn and 48% for Cd, was obtained using the disodium Na_2-EDTA reagent at each maximum concentration 0.25M. As seen in Fig. 5.3, extraction was lower in the Na_4-EDTA solution for all metals, compared to the results obtained with the disodium EDTA, even though the concentration of chelating anion was increased from 0.25 M to 1 M. The lower performance of Na_4-EDTA could be attributed to the alkaline conditions which prevail in the leaching solution using this EDTA salt. The final pH of the pulp was 11.5 using Na_4-EDTA, whereas slightly acidic pHs 5.3 and 4.5 were measured in the pulp of the 1st and 2nd leaching stages with the acidic Na_2-EDTA salt at 0.25M.

The leaching tests using $CaCl_2$-HCl were all carried out at constant total chloride concentration, $Cl^- = 4M$. The initial concentration of HCl was varied between 0.2 and 2 M and the amount of $CaCl_2$ was adapted accordingly to maintain the concentration of chloride ions at 4M. The results obtained during this experimental work (Fig. 5.3), indicate that Pb, Zn and Cd can be completely removed, using a high excess of HCl, at least from this particular soil sample. It should be mentioned however that the extraction rates, exceeding occasionally 100%, were calculated based on the analyses of leachates and do not represent the actual residual concentrations in the treated soils.

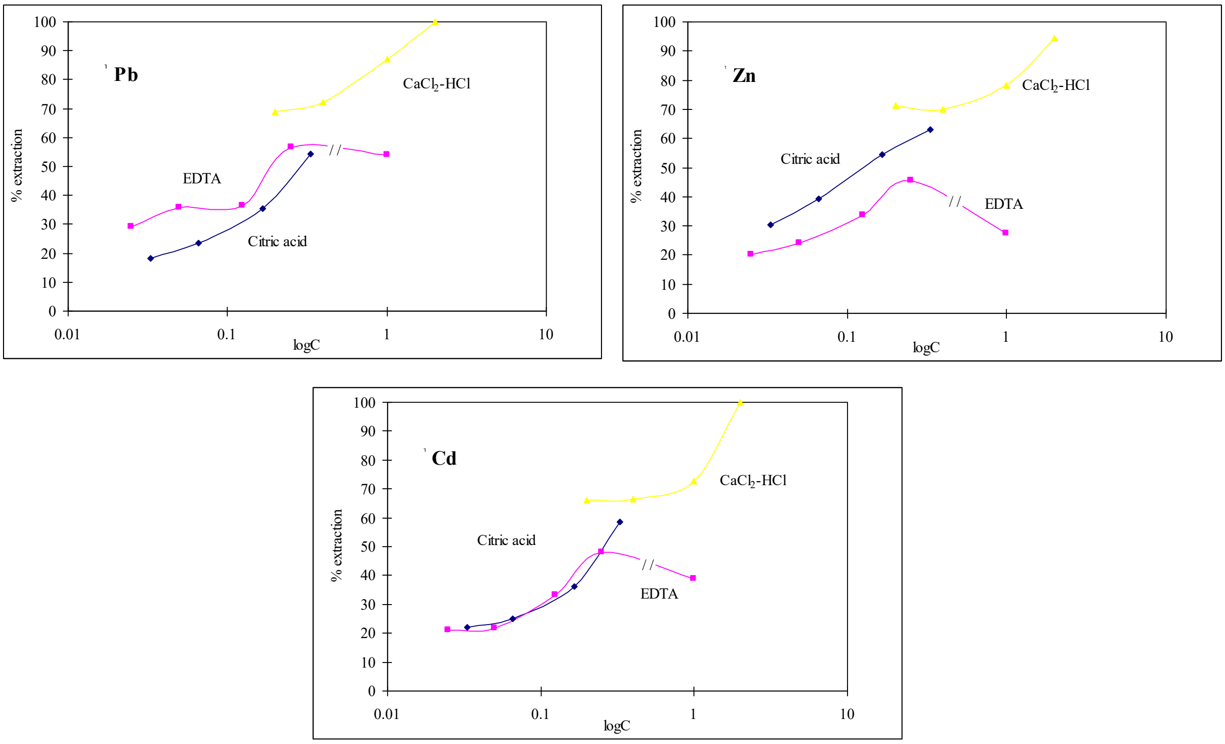


Figure 5.3*. The effect of reagents concentration in the aqueous solution on the removal of Pb, Zn and Cd from the soil sample 802.*

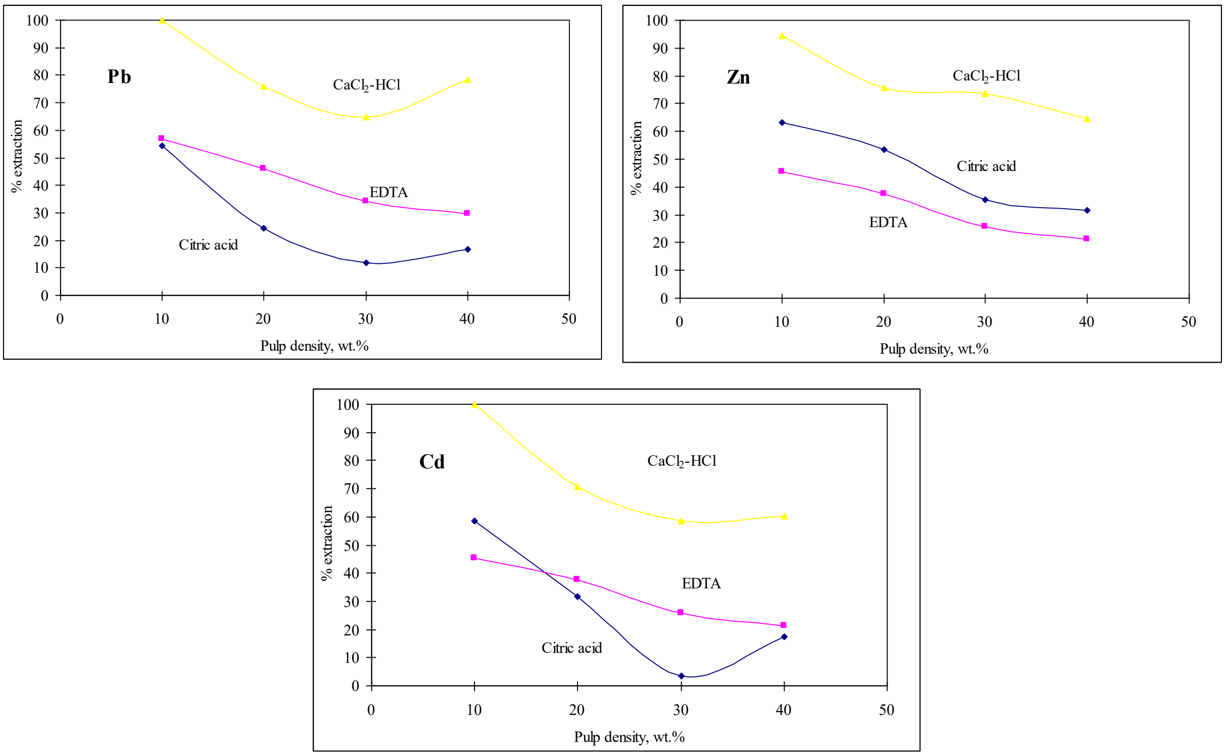


Figure 5.4. *The effect of pulp density on the removal of Pb, Zn and Cd from the soil sample 802.*

The Effect of Pulp Density

In order to investigate whether the dose of reagent per kilogram of soil can be reduced, improving thus the cost effectiveness of the process, a series of leaching tests were conducted maintaining the concentration at the maximum level and increasing the solid to liquid ratio. The tests were carried out on the soil sample 802. Following the same experimental procedure, 2, 4, 6 and 8 grams of the soil (dry basis) were put in the tubes and mixed with a constant solution volume of 20 ml. The resulting pulp densities were 10, 20, 30 and 40 % respectively. Leaching was carried out at two stages, with a three-step washing between the two subsequent leaching stages.

The effect of solid to liquid ratios on the overall extraction is also shown in Figure 5.4. It is obvious that extraction decreases for all the three metals when the solid to liquid ratio increases from 10 to 40%. These results indicate that it is not possible to reduce the dose of reagent decreasing the volume of leaching solution, without affecting the efficiency of metals removal from this particular soil sample.

5.3.4 Agitated Reactors

Experimental Procedure

The experiments in agitated reactors were carried out on the heavily contaminated waste material, G11, from Thoricos bay. The leaching agents which were tested include: acetic acid 1M, oxalic acid 0.5M, citric acid 0.33 M and Na_2EDTA 0.25 M.

The tests were conducted at ambient temperature (22±1ºC). A 400 ml of solution and 40 g of soil were added into a glass spherical stirred reactor. The reactor had a work capacity of 500 ml. The resulting pulp (1:10 solid/liquid ratio) was mechanically agitated at a speed of 500 min^{-1}. After 24 hours, the pulp was filtered and the leach solution was analysed for Pb, Zn, Cd, As, Ca, Mg, Al, Fe_{tot} and Mn. The cake was washed with 1500 ml of water. A second leaching stage under identical conditions was repeated to residue of the first treatment.

In order to obtain kinetic data, systematic sampling of the leach solution was carried out at 15 min, 30 min, 60 min, 2, 3 and 6 hours. The samples after passing through a 0.45μm filter, were analysed for dissolved lead.

Experimental Results

The final extraction percentages for both the contaminants and the major cations of the material are given in Table 5.11. The quality of the residue in terms of toxicity is also shown in Table 5.12.

From the results in Table 5.12 it is obvious that *oxalic acid* is ineffective for the removal of heavy metals but achieves high arsenic extraction rates.

Acetic acid can achieve reasonable extractions of Zn, 64%, and Cd, 100%, but the extraction of Pb is limited 46% and the residue remains toxic with respect to this metal.

The experiments with *citric acid* in agitated reactors gave more promising results. Lead removal from soil, reached a level of 66%. As for the other metals of concern, the extraction rates were 73% for Zn and 92% for Cd. Finally, the residual soil was characterised as non-toxic when subjected to the TCLP procedure, as opposed to the residues obtained from the test tubes experiments. This difference may be due to deficient washing during the test tube experimental procedure.

Leaching with *Na_2EDTA* gave the best results compared to those of acetic and citric acid. The residual soil was characterised as non-toxic. About 80% of total lead in soil was leached (two stages). The reaction rates of other metals were also high: 68% for Zn, 100% for Cd.

The conditions prevailing during the leaching tests were acidic, pH=2.3-4.0 for acetic acid, 1.4-2.8 for citric acid and 4.3-5.8 for Na_2-EDTA. The stoichiometry of $PbCO_3$ dissolution under these conditions can be described with the following reactions:

Acetic acid: $PbCO_3 + CH_3COOH \rightarrow (CH_3COO)_2Pb + CO_2\uparrow + H_2O$

Citric acid: $PbCO_3 + H_3L \rightarrow HPbL + CO_2\uparrow + H_2O$

Na_2-EDTA: $PbCO_3 + Na_2H_2L \rightarrow Na_2PbL + CO_2\uparrow + H_2O$

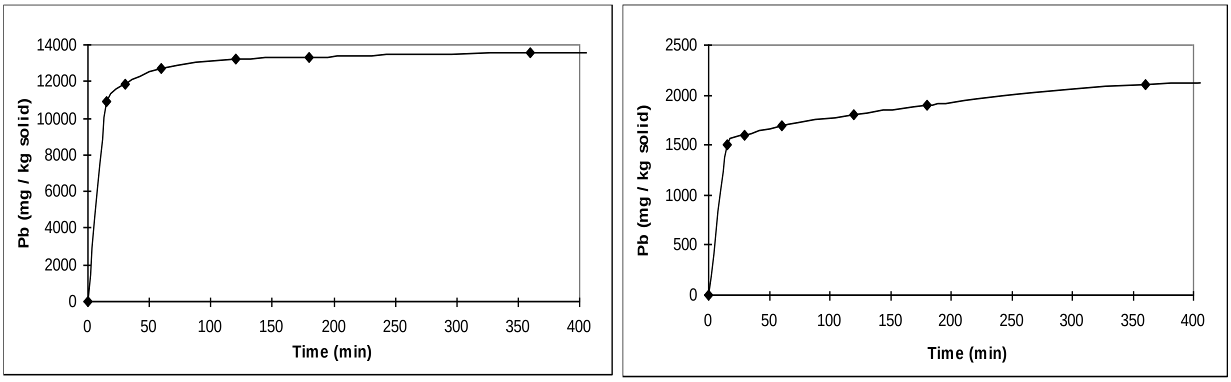
Table 5.11. Removal of contaminants and extraction of major metal cations with various organic acids.

	Pb	Zn	Cd	As	Ca	Mg	Al	Fe_{tot}	Mn
Initial Soil, mg/kg	34800	20200	100	2800	72800	15200	12900	60000	3500
Oxalic acid									
Residue of 1st stage, mg/kg	34608	20162	89	700	72742	4000	6900	20200	1800
Extraction, %	*0.55*	*0.19*	*11.00*	*75.00*	*0.08*	*73.68*	*46.51*	*66.33*	*48.57*
Acetic acid									
Residue of 1st stage, mg/kg	21200	10400	2	2790	27100	9500	12587	59700	2911
Residue of 2nd stage, mg/kg	18700	7200	0	2790	23000	8100	11919	59428	2632
Extraction, %	*46.26*	*64.36*	*100*	*0.36*	*68.41*	*46.71*	*7.60*	*0.95*	*24.8*
Citric acid									
Residue of 1st stage, mg/kg	15800	7800	28	2700	25300	9500	11700	57900	900
Residue of 2nd stage, mg/kg	11800	5500	8	2520	21200	7100	11340	56716	490
Extraction, %	*66.09*	*72.77*	*92*	*10*	*70.88*	*53.29*	*12.10*	*5.47*	*86*
Na_2EDTA									
Residue of 1st stage, mg/kg	8500	9000	4	2210	15500	14229	12091	58300	600
Residue of 2nd stage, mg/kg	7000	6500	0	2070	12700	14178	11882	57469	351
Extraction, %	*79.88*	*67.82*	*100*	*26.07*	*82.55*	*6.72*	*7.89*	*4.22*	*89.97*

Table 5.13. The toxicity of final residue

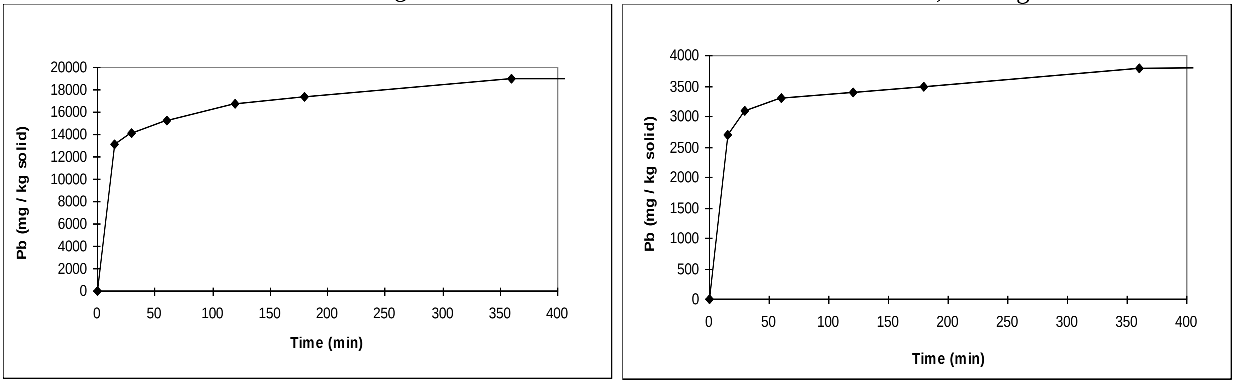
	Concentrations in TCLP leachate, mg/l			
	Pb	Zn	Cd	As
Initial material	**146**	49.6	0.87	<1
Acetic acid residue	**48**	14	0.08	<1
Citric acid residue	4.8	14.6	0.08	<1
Na_2EDTA residue	5.3	25.6	0.17	<1
TCLP limit	5.0	/	1.0	<1

The kinetics of lead removal at the first and second leaching stages is shown in Figure 5.5. From the figures, it can be seen that the major part of Pb is removed within the first hour of leaching. The incremental removal is minimal afterwards especially for the EDTA and the acetic acid systems. The second treatment with fresh leaching solution was found to improve slightly the removal.



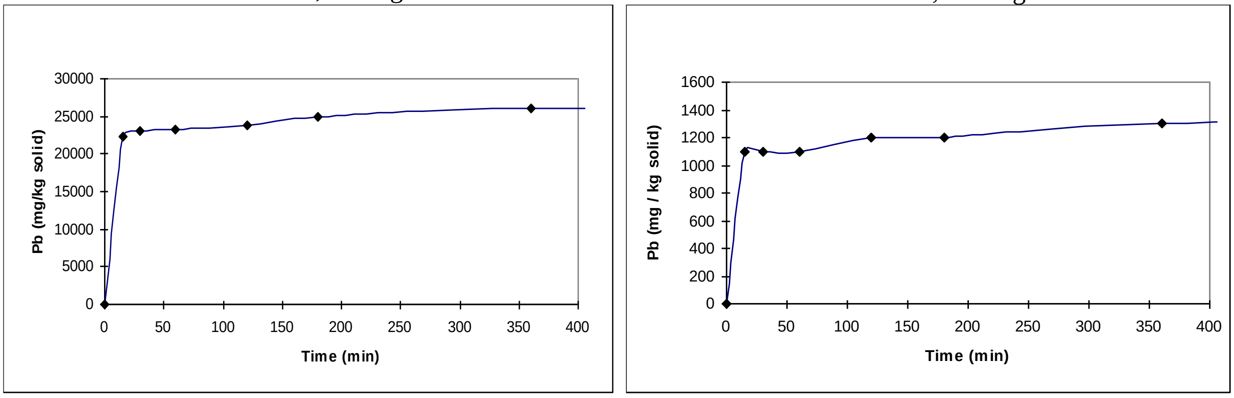
Acetic acid, 1st stage

Acetic acid, 2nd stage



Citric acid, 1st stage

Citric acid, 2nd stage



Na_2EDTA, 1st stage

Na_2EDTA, 2nd stage

Figure 5.5. *Kinetics of lead removal during the treatment of G11 with acetic acid, citric acid and* Na_2EDTA *(2-stages).*

A major disadvantage should be mentioned however for the above leaching systems, affecting their cost-effectiveness and applicability: in addition to metals removal, a substantial dissolution of some important soil components, such as calcite, dolomite and Mn-compounds, was also observed during this experimental work. As seen in Table 5.11 Ca extraction was between 68 and 83% for all reagents tested. Magnesium was mainly attacked by acetic and citric acid and Mn by citric acid and EDTA. The dissolution of Al and Fe was rather limited.

5.3.6 Column Tests

Experimental Procedure

Column tests were carried out on samples from the heavily contaminated wastes at Thoricos bay and Kyprianos site, Savoura. Approximately 100 kg of surface samples (0-10 cm) were collected from the locations corresponding to drillholes G11 (Thoricos bay) and G9 (Savoura). Subsamples from these materials were used for the leaching tests in the columns.

Two leaching solutions were used for each material, EDTA 0.25 M and $CaCl_2$-HCl at a total chloride concentration of 4 M. Preliminary tests were conducted in order to select the optimum HCl acid concentration for the second leaching system. An initial column experiment which was carried out on the material G11 with a strongly acidic solution, HCl=2 M, had resulted in clogging the column due to the precipitation of $PbCl_2$. It should be mentioned that waste G11 has a fine texture (silt loam, 75.6% < -63μm) and a rather limited permeability between 10^{-5} and 10^{-4} cm/s. Following this, shaking flask tests were conducted using high pulp densities 50% and increasing gradually the concentration of HCl acid, in order to select the optimum HCl level. The criterion was to obtain sufficient Pb solubilisation without exceeding the limit of 2000 ppm, which corresponds to the theoretical solubility of $PbCl_2$ at Cl^- 4 M. The concentrations finally selected were 0.25 M for material G11 and 0.50 M HCl for material G9.

The leaching tests were carried out on four columns from Plexiglas, with dimensions 1m height and 10 cm diameter. A 10 cm layer of silica sand, between two layers of fibreglass was placed to the bottom of each column in order to prevent washing off of fine particles. Fiberglas was also added to the top surface of the material to homogenise the penetration of leaching solutions.

Details about the characteristics of the four columns and the experimental conditions are presented in Table 5.13.

Leaching solutions were fed with pumps from a 4 litre tank to the top of the columns, at a flowrate slightly below their permeability, 0.5-0.7 l/d for G11 and 7.5-8.0 l/d for G9. A different procedure has been followed for the two materials due to their different permeability, regarding solution supply. Leaching solution was recycled for Savoura wastes, G9, in order to increase contact time and maximise the utilisation of reagents. The criterion for solution renewal was pH stabilisation. Recycling was not applied for Thoricos Bay tailings, G11.

Experimental Results

Column Treatment of G11 and G9 with the Na_2EDTA Leaching System

Percent extraction of contaminants and major metal cations during the column treatment of wastes G11 and G9 is shown in Figure 5.7. The extractions are presented as a function of the amount of EDTA solution (0.25 M) fed to the columns per kg of material.

A total of 56 and 68 litres of solution were supplied in the columns containing G11 and G9, respectively. Per kilogram of treated material, this amount corresponds to 16.8 litres of solution and 4.2 moles of EDTA for G11. Approximately the same quantities, 17.4 litres and 4.4 moles of EDTA, were used per kilogram of G9.

The sequence of metals extraction, as shown in the figures, indicates clearly the selectivity of EDTA, primarily for Pb and secondarily for Cd and Zn, and follows approximately the values of the corresponding chelate formation constants:

Sequence of metals release: Pb > Cd > Zn > Mn > Ca > Mg

Chelate form. const., log K_{ML}: 17.9 > 16.3 ~ 16.4 > 13.9 > 12.4 > 10.6

Extraction of iron, Fe, was rather limited not exceeding 12%, though the chelate formation constants with Fe(II) and Fe(III) are high, 16.1 and 27.7 respectively. It is reported in the literature (McCrary 1982) that the formation of Fe(III)-chelates is often hindered by kinetic limitations. Moreover, these chelates are unstable at pH>5 due to the precipitation of $Fe(OH)_3$. These are probably the reasons for the low extraction of iron, which occurs mainly in the form of Fe(III) oxides, such as limonite, goethite etc.

Table 5.13. Column experiments

Leaching Solution	Thoricos Bay Tailings G11		Savoura Wastes G9	
	EDTA 0.25M	$CaCl_2$-HCl C_{HCl} 0.25 M	EDTA 0.25M	$CaCl_2$-HCl C_{HCl} 0.5 M
Geotechnical characteristics of the material				
Texture	Silt loam, 76.5% < 63μm		Loamy sand, 17.9% < 63μm	
Particle density (g/cm^3)	2.58		2.83	
Bulk density (g/cm^3)	1.4		1.88	
In situ permeability (cm/s)	5.1E-04		2.4E-03	
Column characteristics				
Diameter (cm)	10	10	10	10
Weight of material (kg)	3.335	5.365	3.900	4.330
Height of material (cm)	31	50	35	39
Volume of material (cm^3)	2434	3925	2748	3062
Porosity (cm^3)	1146	1847	1370	1532
Init. water retention V_w (ml)	1080	1740	1000	1140
Permeability in columns K_s (cm/s)	9.91E-05	7.37E-05	1.11E-03	1.18E-03
Procedure				
Solution supply (4 Liters)	One pass		Recycling up to pH stabilisation	
Solution Flowrate Q_w (l/d)	0.672	0.5	7.5	8
Duration of experiments				
Days	80	400	260	300
Total amount of solution and reagents added in the columns				
Liters	56	128	68	120
EDTA/HCl (mole/kg)	4.18	7.27	4.35	13.9

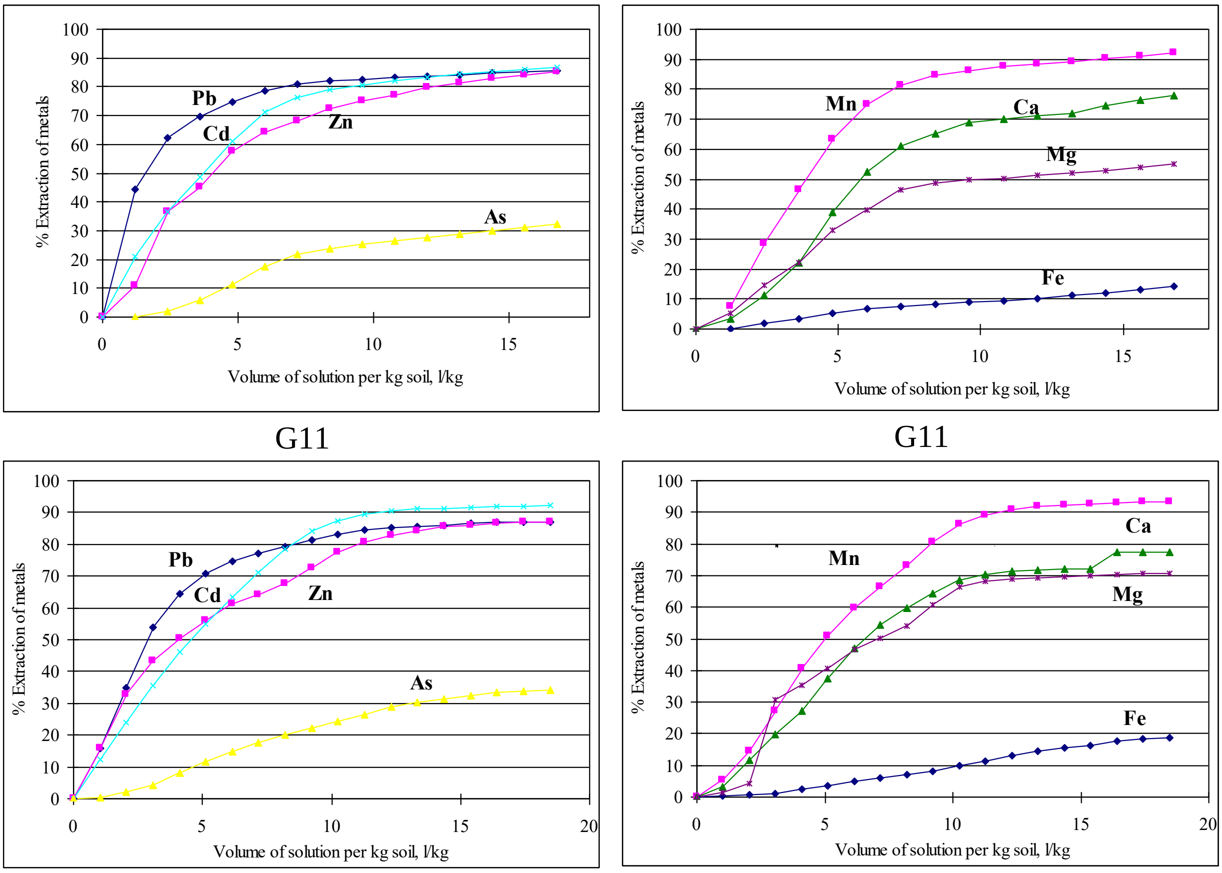
Arsenic, as an oxyanion in the aqueous solutions, does not form chelates with EDTA. It is mainly released through the dissolution of related arsenate phases. As already discussed in §5.2.2 (Table 5.2b) many Pb-arsenate and Pb-Fe-arsenate phases have been identified in Lavrion soils and wastes. It is however seen that, although more than 85% of Pb is extracted, arsenic removal doesn't exceed 35%. The following explanations may be suggested for this behaviour: a) the greater percentage of As is bound in the form of sulphides, *i.e.*, FeAsS, which are not soluble in EDTA and b) Pb-arsenates are dissolved and As co-precipitates with Fe(III) in highly insoluble iron-arsenate compounds (Kontopoulos *et al.* 1988). The fate of the arsenic and iron compounds during the EDTA treatment will be elucidated with the mineralogical analyses of the residues, which have been planned for the following months.

The pH of the resulting elution is initially alkaline, around pH=8, suggesting that all the acidity of the initial reagent is consumed, through dissolution reactions of the kind:

$$PbCO_3 + Na_2H_2L \rightarrow Na_2PbL + CO_2 \uparrow + H_2O$$

As reactions proceed, the pH declines gradually towards pH 4.5, indicating partial utilisation of the reagent.

The trend of the curves in Figure 5.6 suggests that sufficient extraction of metals can be obtained supplying approximately 12 litres of solution or 2.5 moles of Na_2EDTA per kg of material.



G11 G11

G9 G9

Figure 5.6. *The extraction of contaminants and major metal cations, during the column treatment of material G11 and G9 with EDTA 0.25 M.*

Column Treatment of G11 and G9 with the $CaCl_2$-HCl Leaching System

Percent extraction of contaminants and major metal cations during the column treatment of wastes G11 and G9 with $CaCl_2$-HCl is shown in Figure 5.8. The extractions are presented as a function of the amount of solution (0.25M HCl for G11 and 0.5M HCl for G9) fed to the columns per kg of material.

A total amount of 128 litres of solution corresponding to 7.3 moles of HCl per kg of material were supplied in the column containing G11. The corresponding quantities for G9 were 120 litres of solution and 13.9 moles of HCl per kg of material.

The sequence of metals extraction, and more particularly the sequence of Pb release, was slightly different between materials G11 and G9, when treated with this leaching system:

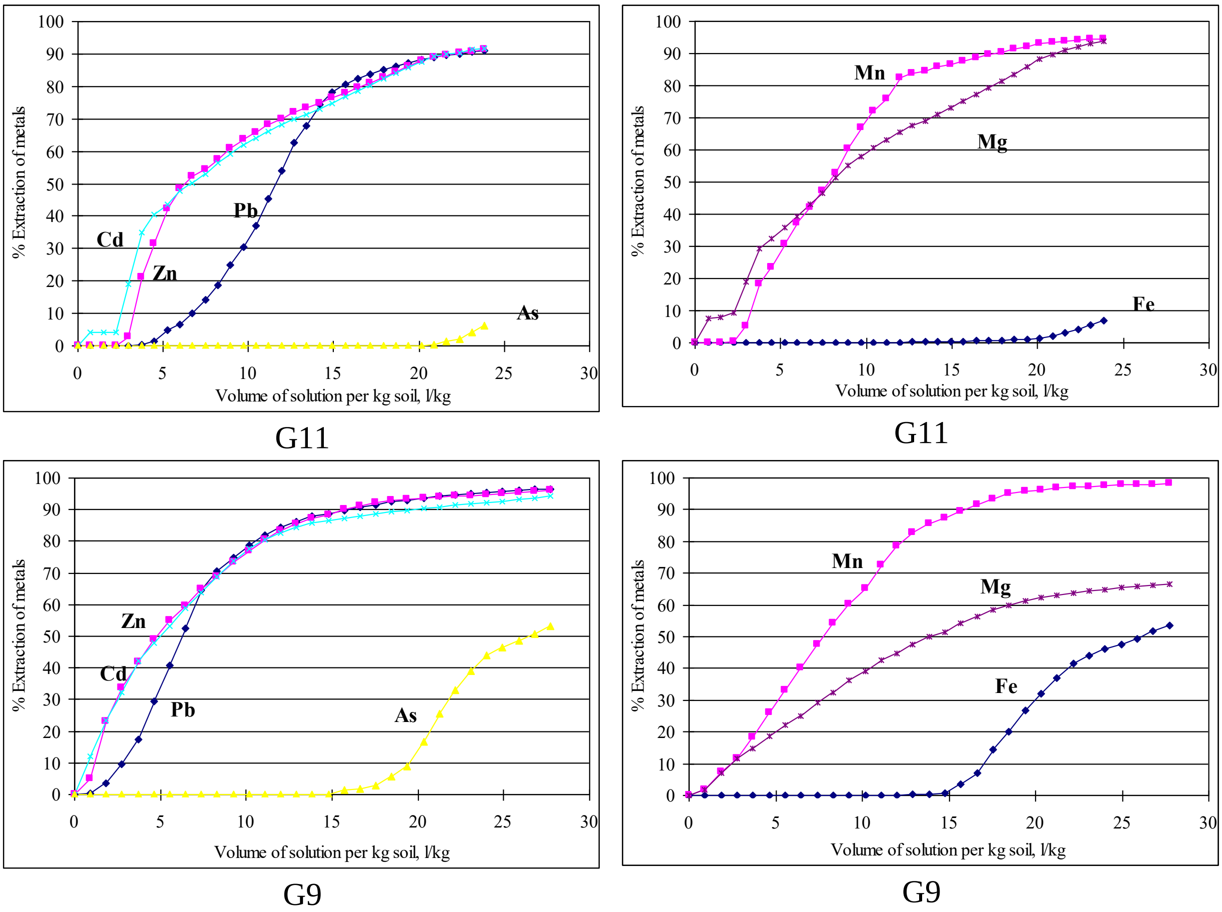
G11 : Cd ~ Zn > Mn ~ Mg > Pb > Fe ~ As

G9 : Cd ~ Zn > Pb > Mn > Mg > Fe ~ As

High concentrations of Pb, up to 4900 mg/l in G11 and 3500 mg/l in G9, were measured in the leachates for both materials. These concentrations exceed clearly the theoretical solubility of $PbCl_2$, which was calculated to be approximately 2400 mg/l at Cl_T=4 M. These oversaturation conditions may result in the precipitation of $PbCl_2$ inside the columns, which is subsequently redissolved and washed out, as suggested by the high extraction rates achieved finally, 92% for G11 and 97% for G9. This process is probably more slow for the material of low permeability G11.

The removal of iron and arsenic follows a similar trend and occurs only when the solution pH becomes strongly acidic, pH<1.

The abrupt pH drop takes place following the addition of about 5.5 moles of HCl per kilogram of material, for both G11 and G9. This amount corresponds approximately to the Neutralisation Potential of the wastes, as estimated applying the Sobek technique (1978): NP=224 kg $CaCO_3$/t for G11 and 277 kg $CaCO_3$/t for G9.



G11 G11

G9 G9

Figure 5.8. *The extraction of contaminants and major metal cations, during the column treatment of material G11 and G9 with $CaCl_2$-HCl.*

The Overall Performance of Na_2EDTA and $CaCl_2$-HCl

The total extraction of metals from these heavily contaminated materials, using Na_2EDTA and $CaCl_2$-HCl, was calculated based on the chemical composition and residual weight of final residues and is presented in Table 5.14. It is mentioned that calculations based on the chemical analyses of leachates gave total removal rates exceeding in several cases 100% for Pb, Zn and Cd. A correction factor, taking into consideration the residual concentrations in the treated material, was used for the calculation of the extraction curves presented in the previous figures.

Comparing the results obtained with the two leaching systems the following conclusions are drawn.

1. Both leaching systems can achieve very high removal rates for Pb, Zn and Cd exceeding 87%.
2. Best results were obtained with the acidic brine $CaCl_2$-HCl, with extraction rates up to 97% for Pb, Zn and Cd.
3. Treatment with $CaCl_2$-HCl can even reduce the concentrations of the above heavy metals near the international standards for industrial use of land. In order to obtain such low residual concentrations a high excess of HCl is required, as seen from the results obtained on material G9 which was treated with 13.9 moles HCl/kg, compared to 5.5 moles which are required to consume the inherent Neutralising Potential.
4. Despite the strong chelating capabilities of Na_2EDTA it was not possible to obtain such low residual concentrations. This suggest that some species of Pb, Zn, and Cd are refractory to chelation and can be dissolved only under strongly acidic conditions.
5. Arsenic is extremely immobile at least with the leaching systems tested during this experimental work. Alkaline treatment or elektrokinetic techniques may be more appropriate for this particular element.
6. Both leaching systems attack the soil matrix and result in the dissolution of important metal components, such as Mn, Ca and Mg. This result in a substantial weight loss ranging between 44 and 49 % for Na_2EDTA and 17 and 38 % for $CaCl_2$-HCl.

Interference of $CaCO_3$ dissolution in reagents consumption

It is often reported in the literature that the major advantage in using chelators, and especially EDTA, for the decontamination of soils is that they remove selectively the heavy metals and preserve the integrity of soil matrix. During this research work it was found that important soil components are also dissolved. This fact results in a very low degree of EDTA utilisation and affect seriously the cost effectiveness of the process.

A solution, produced during the test tube experiments with sample 802, was analysed for its content in Ca, Mg, Al, Fe and Mn in order to estimate the degree of simultaneous dissolution of soil compounds, such as $CaCO_3$, Al-Fe-Mn oxides etc. The chemical analyses are presented in Table 5.17. Due to the strong affinity of EDTA chelant with the above metals, it was assumed that the soluble metal levels as determined by atomic adsorption are practically equivalent to the corresponding 1-1 metal chelate (ML). The percentage of each metal chelate (ML) with respect to total available EDTA (L_T) is also given in Table 5.17.

Table 5.16. Weight loss and chemical composition of final residues

	Initial material	Treatment residue	Removal %	Initial material	Treatment residue	Removal %
Na_2-EDTA						
		G11			**G9**	
Weight (kg)	3.335	1.690	49	3.900	2.169	44
Metals	*mg/kg*	*mg/kg*		*mg/kg*	*mg/kg*	
Pb	33700	7550	89	25900	6600	86
Zn	19360	5070	87	20850	4970	87
Cd	120	25	89	160	20	93
As	2800	2950	47	2600	2450	48
Mn	3700	500	93	4600	600	93
Mg	11650	10900	53	8600	5700	63
Ca	89550	40550	77	108400	53400	73
Fe	55100	69450	36	60250	70800	35
Al	15450	22300	27	14950	23050	14
$CaCl_2$/HCl						
		G11			**G9**	
Weight (kg)	5.365	4.125	23.1	4.330	2.696	38
Metals	*mg/kg*	*mg/kg*		*mg/kg*	*mg/kg*	
Pb	33700	3710	92	25900	1100	97
Zn	19360	2190	91	20850	1280	96
Cd	120	16	90	160	8	97
As	2800	3600	1	2600	1500	64
Mn	3700	250	94	4600	100	99
Mg	11650	2690	83	8600	750	95
Ca	89550	7.440	92	108400	46950	73
Fe	55100	77400	(-1)	60250	50800	47
Al	15450	10760	47	14949	11100	54

Standards for soil quality

Metals, mg/kg	Dutch Intervention Values	Canadian: Industrial Land Use
Pb	530	600
Zn	720	360
Cd	12	22
As	55	12

Table 5.17. Concentration of metals and distribution of metal chelates in the EDTA solution (Test tube experiments, sample 802, first leaching stage, 30% pulp density)

Metals	Formation constants of metal chelates $\log K_{ML}$	Concentration in the leachate mg/l	Percentage of chelant bound with metal M %
Cd	16.28	4.0	0.01
Mn	13.87	53.3	0.43
Al	18.90	27	0.44
Fe	16.10	66.6	0.52
Mg	10.60	110	1.97
Pb	17.88	***956***	***2.01***
Zn	16.44	***565***	***3.77***
Ca	12.40	***8160***	***88.73***
		Total, %	***97.87***

As seen in the table, the distribution of metal chelates in solution does not follow the values of formation constants, since it is also determined by the relative abundance and availability of metals in the soil. Calcium is the predominant dissolved element in the solution, binding almost 89 % of the available EDTA, while Zn and Pb utilise only 5.7 % of the chelate ions.

Based on these results, it was concluded that predictions for EDTA consumption must be based on the Ca content of the soil, rather than on the contamination level with respect to heavy metals. In Fig. 5.8 the combined extraction of Pb, Zn and Cd (HM) is compared to the simultaneous dissolution of Ca. This figure summarises all the data obtained at different EDTA concentrations, pulp densities and successive leaching stages. The results are expressed as a function of the molar ratio of EDTA with respect to the initial Ca and heavy metals (HM) content of the soil (3000 mmol/kg and 217 mmol/kg respectively). It is seen that in order to obtain maximum heavy metals recovery (50%), Ca must be also removed at a high percentage (71%). At these conditions, the EDTA/HM molar ratio was 23, while the corresponding EDTA/Ca molar ratio was 2.0, indicating that Ca provide a more realistic basis for consumption calculations.

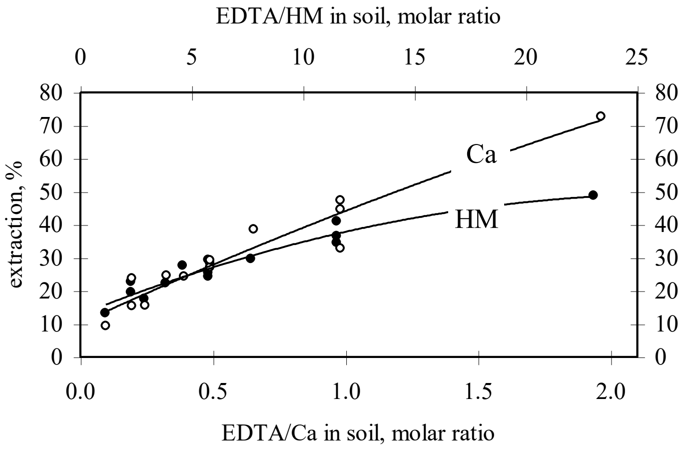


Figure 5.8. *Extraction of heavy metals (HM) and Ca as a function of the EDTA/Ca and EDTA/HM molar ratios. Data obtained at different EDTA concentrations, pulp densities and successive leaching stages (test tubes experiments).*

Regarding the $CaCl_2$-HCl mixture, it is not possible to avoid dissolution of $CaCO_3$, since the major mechanism involved in metals release with this leaching system is pH reduction, which affects both contaminants and carbonate minerals. This is however a very efficient system, combining two major advantages: a) it is based on the use of low cost reagents, b) the final liquid effluent of the process contains mainly $CaCl_2$ which is acceptable for disposal in natural receivers, *i.e.*, sea.

5.4 INVESTIGATION OF INTEGRATED LEACHING PROCESSES

5.4.1 Introduction

The successful implementation of leaching processes does not only rely on the efficient removal of metals from soils. An integrated process includes additional treatment stages, which must be optimised in order to obtain a soil remediation technique environmentally and economically acceptable:

a) Metals should be removed from the leachate and recovered in the form of a low volume solid residue, appropriate for disposal in a hazardous waste landfill area or even for processing in the metallurgical industry.
b) in most cases the leaching solution, should be further treated
- for regeneration and reuse in the leaching stage, or
- for final polishing in order to produce an acceptable liquid effluent for disposal in natural waters.

For the leaching systems which are based on the use of organic acids and chelators, it was thought more appropriate to investigate process flowsheets comprising *complete regeneration and recycling* of the leaching solution. It is thus possible to avoid production of liquid effluents with a high organic load which are not likely to be accepted for final discharge. Moreover such a process has the benefits of reagents cost saving which is mainly crucial for the case of EDTA.

Total recycling is not possible for the HCl-$CaCl_2$ system. Fresh HCl should be supplied to compensate the consumption of acidity and a liquid stream must be discarded to maintain the mass balance. This bleed stream should satisfy the environmental regulations for disposal, and a final polishing step is probably required.

The crucial unit operations included in the above processes were studied experimentally and the results are discussed in the following paragraphs.

5.4.2 Experimental Procedure

Overview of the testwork

The experimental work undertaken for the development of the integrated leaching process is summarised in Table 5.16. Resin adsorption and precipitation techniques have been evaluated for the removal of heavy metals from the leachates. Experiments were also conducted for the regeneration of Na_2H_2EDTA reagent following the removal of heavy metals and for the final polishing of the chloride effluent in the corresponding processes.

Table 5.16. Overview of the laboratory testwork

A. REMOVAL OF HEAVY METALS FROM THE LEACHATE

	CITRIC ACID	Na_2-EDTA	$CaCl_2$-HCl
Resin adsorption			
Strongly acidic	+		
Weekly acidic		+	
Precipitation			
NaOH	+	+	
$Ca(OH)_2$	+		+
Na_2S		+	

B. SUBSEQUENT TREATMENT STAGES

	CITRIC ACID	Na_2-EDTA	$CaCl_2$-HCl
Regeneration of leaching solution		+	
Final polishing of liquid effluent			+

Resin Adsorption

A strongly acidic cationic resin (DOWEX 50WX8) was used for the removal of heavy metals from the citric acid leach solutions. Strongly acidic cation exchangers have sulphonic acid groups and can be used in the whole practically available pH-region down to pH=1.

The resin comprised of particles in the diameter range of 0.1-0.3mm, had moisture content of 46.7% and its capacity was 1.9 eq/L. The laboratory scale column had a volume of approximately 20 ml, corresponding to a total capacity of 38meq.

For the case of Na_2EDTA leach solution, the strongly acidic cationic resin was inappropriate, as it led to EDTA acid precipitation. A weakly acidic cationic resin was used (DOWEX CG-5OI). These cation exchangers carry carboxylic groups and they can treat alkaline and neutral solutions down to pH=5. The size of the particles ranged from 0.075 to 0.150mm. The resin had moisture content of 50-55% and its capacity was 3.5 eq/L. The column prepared in the laboratory had a volume of approximately 10 ml, corresponding to a total capacity of 35 meq.

Test were carried out with the following procedure: Twenty (20) ml of the leach solution were applied to the column at a constant flowrate (~2 cm/min for the strongly acidic and 1 cm/min and the weekly acidic resin). Resin was then washed with 40ml of water. The elute was diluted to a final volume of 100ml and analysed with AAS.

Following the completion of the test, resin was regenerated with HCl and washed with the appropriate amount of water.

Precipitation techniques

The following reagents were used for the precipitation experiments:

- NaOH for the citric acid and Na_2EDTA solutions
- $Ca(OH)_2$ for the citric acid, EDTA and $CaCl_2$ solutions, and
- Na_2S for the Na_2EDTA leach solutions.

The experiments were carried out in beakers at atmospheric conditions and under continuous agitation with a magnetically driven stirrer. The precipitation reagents are added to the solution stepwise at predetermined quantities. Following the addition of each dose, the solution / suspension is left in agitation for 15 min, the pH of the solution is recorded and an aliquot is taken to determine the residual concentration of metals.

5.4.3 The Citric Acid Process

Removal of metals from the leachate

The results concerning the removal of metals from the citric acid leach solution are shown in Tables 5.17, 5.18 and 5.19. The cation exchange treatment was found to remove efficiently the metals from the leach solution. Precipitation with NaOH was inefficient; a very high excess of NaOH, 6.5 greq/L, was required in order to observe the initial formation of precipitates. Better results were obtained using lime. An amount approximately equivalent to the normality of the solution, 1.1 greq/L $Ca(OH)_2$, was sufficient to remove more than 99% of all the metals examined.

Table 5.17. Treatment of the citric acid leachate with a strongly acidic resin (DOWEX 50WX8)

	(mg/l)							
	Pb	Zn	Cd	Ca	Mg	Al	Fe	Mn
Initial citrate sol.	1900	1240	7,18	4750	570	120	210	260
Treated citrate sol.	bdl	bdl	bdl	0,1	bdl	bdl	bdl	bdl
Removed %	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0

Table 5.18

Precipitation of metals from the citric acid leachate with NaOH

NαOH (greq/L sol.)	pH	(mg/l)								
		Pb	**Zn**	**Cd**	**As**	**Ca**	**Mg**	**Al**	**Fe**	**Mn**
0	2,8	1900	1240	7,2	10	4750	570,0	120,0	210,0	260,0
6,53	>12,5	760	1000	0,2	0				21,4	14,8
7,57	>12,5	900	1140	0,5	4	240	40,2	29,8	1,8	5,6

Table 5.19. Precipitation of metals from the citric acid leachate with Lime

$Ca(OH)_2$ (greq/L sol.)	pH	(mg/l)							
		Pb	**Zn**	**Cd**	**As**	**Mg**	**Al**	**Fe**	**Mn**
0	2,8	1900	1240	7,2	10	570,0	120,0	210,0	260,0
1,09	-	13	8	0,1	0	5,4	32,1	0,5	1,7
2,18	-	16	9	0,1	0	4,2	28,7	8,0	1,1
3,27	-	15	9	0,0	0	5,5	31,0	9,3	1,0

Conceptual Flow Diagram

The use of a strongly acidic cationic resin for the removal of metals from the citric acid leach solution seems to be a promising alternative, as it gives removal rates near 100%. Moreover the product is a regenerated acid solution that can be recycled directly to the leaching stage. A conceptual flow diagram is given in Figure 5.9

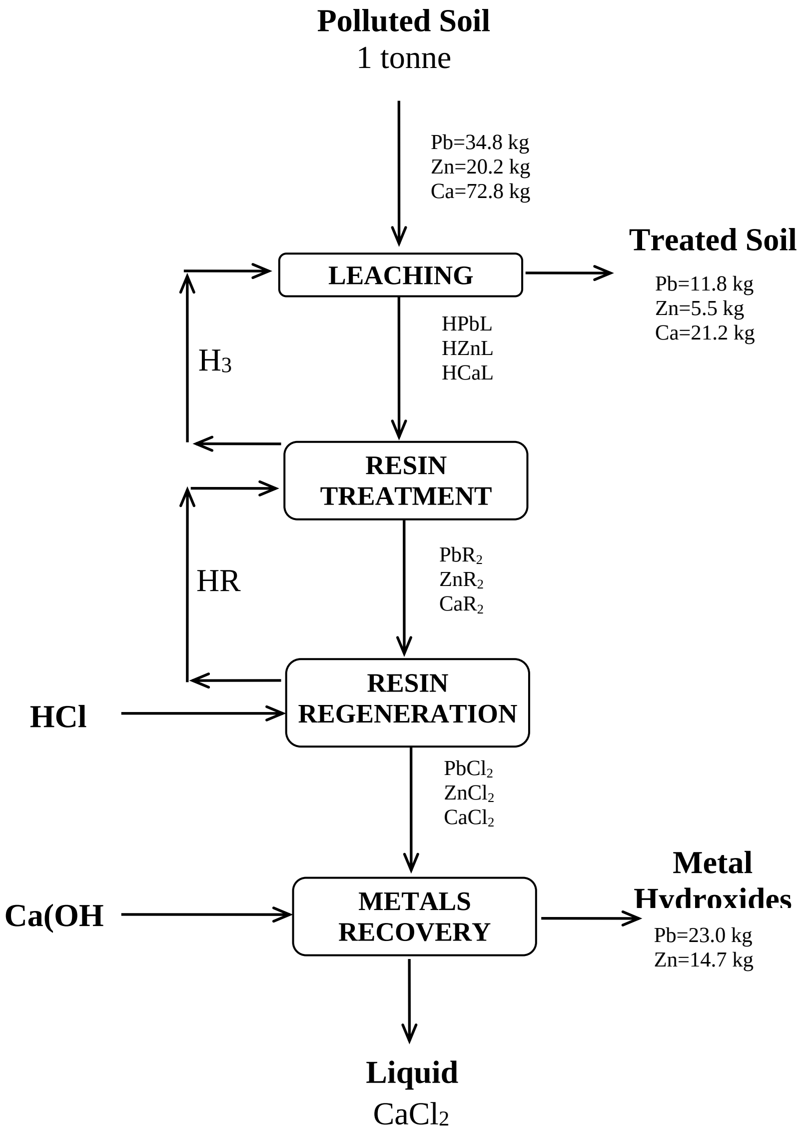


***Figure 5.16**. Conceptual flow diagram for a leaching process based on the use of citric acid*[2]*.* *H_3L: citric acid, HR: Strongly acidic resin.*

This process comprises four treatment steps:

1. Leaching of the contaminated material
2. Removal of metals from the leachate with resin treatment and recycling of the regenerated leaching solution
3. Regeneration of the strongly acidic resin with HCl
4. Recovery of the metals from the HCl solution by precipitation with $Ca(OH)_2$.

---

[2] The indicative mass balance of metal cations corresponds to the experimental results obtained during the treatment of waste G11 with citric acid (agitated reactors).

Based on this simplified flowsheet, the main reagents consumed in the process are HCl and $Ca(OH)_2$, for the regeneration of the resin and the precipitation of the metals. The final effluents are the sludge of metal hydroxides and the $CaCl_2$ solution, produced during the fourth step.

5.4.4 The Na_2EDTA Process

Removal of metals from the leachate

Resin Treatment

A weakly acidic cationic resin (DOWEX CG-5OI) has been tested for the removal of heavy metals from the Na_2EDTA solution. The results are shown in Table 5.22. It is evident that this treatment is inefficient; the metal-EDTA chelates are very stable and cannot be broken with cation exchange mechanisms.

Table 5.20. Treatment of the Na_2EDTA leachate with a weakly acidic resin(DOWEX CG-5OI)

	(mg/l)				
	Pb	Zn	Cd	Fe	Mn
Initial Na_2EDTA sol.	2630	1120	9,63	170	290
Treated Na_2EDTA sol.	2610	980	8,84	161,5	280
Removed %	0,80	12,50	8,300	5,00	3,40

Precipitation of metals

Neutralisation of the EDTA leach solution with NaOH, up to pH values greater than 13.5, was inefficient for the precipitation of heavy metals (Table 5.23). Only arsenic and iron were efficiently removed, probably as ferric arsenate, at pH values below 12.

Table 5.23. Precipitation of metals from the Na_2EDTA leachate with NaOH

NaOH (greq/L sol.)	**pH**	(mg/l)								
		Pb	**Zn**	**Cd**	**As**	**Ca**	**Mg**	**Al**	**Fe**	**Mn**
0,00	5,3	2630	1120	9,63	59,0	5730	97,1	80,9	170,0	290,0
0,11	12,2	2603	1069	8,79	0,0	4852	62,3	56,4	4,9	277,6
0,16	12,8	2590	1050	8,84	6,2	4878	62,7	57,2	7,4	270,4
0,32	13,3	2506	1102	8,46	0,0	5170	59,2	69,5	6,4	237,6
0,48	>13,5	2498	1060	8,47	4,5	4961	56,0	73,6	4,8	168,0
1,00	>13,5	2470	1050	9,45	55,0	5020	35,7	75,9	5,5	190,0
2,00	>13,5	2400	1100	8,54	39,0	5050	21,9	70,2	7,0	110,0
4,00	>13,5	2290	1030	8,98	45,0	4890	1,1	69,8	16,2	94,1
6,00	>13,5	2200	990	8,74	39,0	4580	0,6	65,5	31,0	110,0

Because of the inefficiency of precipitation as hydroxides, sulphide precipitation with sodium sulphide was tested. A typical precipitation reaction is:

$Na_2PbL + Na_2S \rightarrow PbS (s) + Na_4L$

The results are presented in Table 5.22 and Figure 5.10. It is seen that lead, zinc, and cadmium, can be very efficiently removed, while calcium is partially precipitated. It was found however that sulphide precipitation is inappropriate for arsenic, since all the initial concentration remained in solution.

Table 5.22. Precipitation of metals from the Na_2EDTA leachate with Na_2S

Nα$_2$S (mole/L sol.)	(mg/l)							
	pH	**Pb**	**Zn**	**Cd**	**As**	**Ca**	**Fe**	**Mn**
0	5,2	2800	1063,0	8,80	58	5770	150,0	270
0,05	8,4	0	997,5	0,27	58	4190	147,0	268
0,1	9,7	0	968,0	0,32	58	4059	143,0	269
0,15	12,0	0	84,1	0,33	58	4082	125,7	266
0,2	12,6	0	3,6	0,38	57	4104	96,5	269
0,25	12,8	0	2,0	0,45	58	4112	90,6	268
0,3	12,9	0	1,8	0,53	58	4290	52,5	265

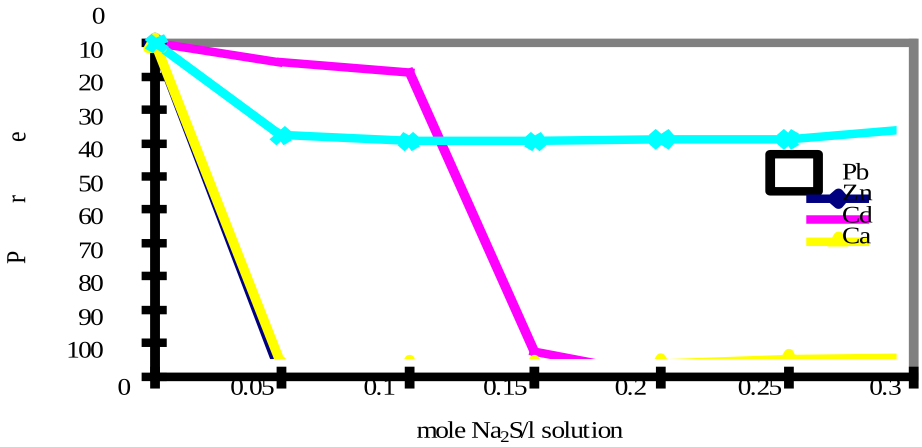


Figure 5.10*. The precipitation of major heavy metals and calcium from the EDTA leach solution by the addition of Na_2S.*

Table 5.23. A two-step treatment of the Na_2EDTA solution with $Ca(OH)_2$ and Na_2S for the removal of metals

Addition $Ca(OH)_2$ moles/l	Addition Na_2S moles/l	pH	Concentrations in the solution								
			Pb (ppm)	Zn (ppm)	Mg (ppm)	Cd (ppm)	As (ppm)	Ca (ppm)	Fe (ppm)	Al (ppm)	Mn (ppm)
0		5.82	2851	1570	320	10.68	83.7	5875	385	114.6	319
0.019		7.20	2557	1426	293	9.94	75.9	5921	344	103.5	289
0.024		8.46	2528	1387	289	9.73	75.2	5901	335	69.6	279
0.041	0	10.33	2399	1248	92.5	8.92	3.1	6019	133	16.4	261
	0.007	11.00	2000	1203	98.6	6.47	4.3	5893	93.4	14.7	260
	0.039	12.00	785	1272	92.2	2.74	5.5	4789	0.9	16.0	271
	0.109	12.64	301	137	97.8	0.92	6.5	6575	0.5	15.5	249

The above results indicate that a two step precipitation technique should be applied for the efficient removal of all toxic elements: addition of NaOH or $Ca(OH)_2$ for the removal of arsenic, followed by the addition of Na_2S for the precipitation of heavy metals. Experimental results, obtained with this treatment scheme are shown in Table 5.23.

Regeneration of the leaching solution after metals removal

Recycling is crucial for EDTA due to the high cost of this reagent. The solution, emanating from the leaching stage, contains all the metals extracted from the soil, such as Pb, Zn, Cd etc., and eventually residual H^+. During the precipitation treatment, for instance with NaOH and Na_2S, the residual acidity is neutralised and the metal cations are removed from the solution and replaced by Na^+ ions. The resulting solution is strongly alkaline and contains an excess of Na^+ ions in comparison with the initial leaching reagent. The regeneration of the initial acidity could be achieved using a weakly acidic resin. The typical reaction is given below:

$$Na_4L + 2\ HR_w \rightarrow Na_2H_2L + 2\ NaR_w$$

A test was carried out on the EDTA solution emanating from the Na_2S precipitation treatment. The results are presented in Table 5.24 and Figure 5.11. As seen, the resin adsorbs the excess of Na^+ ions and the initial acidity is partially regenerated. The resulting solution contains 0.35 greq/L of H^+, against 0.5 greq/L of the original. It should be mentioned that the carboxylic resin used in this test cannot reduce the pH below 5, which is slightly higher compared to the pH=4.3 of the original solution. This treatment does not affect the Ca^{2+} ions remaining in the solution following the precipitation stage. Forty percent (40%) of the EDTA in the final solution remains associated with calcium.

It is pointed out that the resin treatment step is mainly required in order to avoid the accumulation of Na^+ ions in the closed circuit. Moreover, this treatment can regulate the pH of the recycled solution around 5. The leaching experiments suggest that this slightly acidic environment is essential in order to accelerate the kinetics of Zn dissolution and maximise the extraction of Pb up to 90%.

Table 5.24. Composition of the EDTA solution in mol/l in the initial stage, after precipitation and after regeneration stage.

	Initial	After precipitation	After regeneration
Na_2H_2L	0.25		0.10
NaH_3L			0.05
Na_2CaL		0.10	0.10
Na_4L		0.15	
Na_2S		0.15	

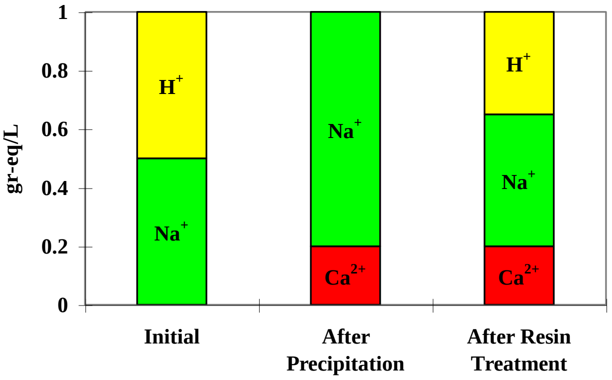


Figure 5.11. *Distribution of cations in the EDTA solution in the successive treatment stages.*

Conceptual flow diagram

A conceptual flow diagram for the case of EDTA is given in Fig. 5.12. This process comprises the following treatment steps:

1. Leaching of the contaminated material
2. Removal of metals from the leachate by precipitation with NaOH and Na_2S
3. Regeneration of the initial acidity with a weekly acidic resin and recycling of the solution to the leaching stage
4. Regeneration of the resin with HCl

Based on this simplified flowsheet, the main reagents consumed in the process are NaOH and Na_2S for the precipitation of the metals and HCl for the regeneration of the resin. The final effluents are the sludge of metal sulphides / hydroxides and the NaCl solution, produced during resin regeneration.

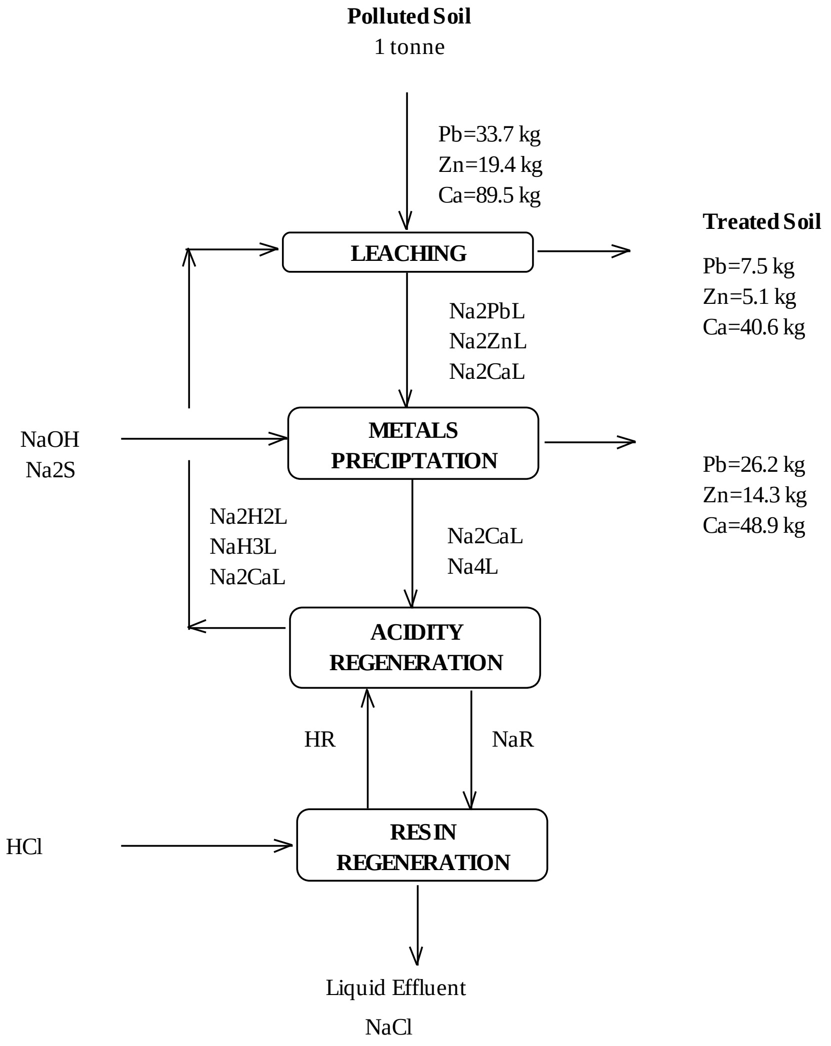


***Figure 5.19**. Conceptual flow diagram comprising the precipitation of metals and the regeneration and recycling of the leaching solution. HR: Weekly acidic resin.*

5.4.5 The HCl-$CaCl_2$ Process

Removal of metals from the leachate

The selection of $CaCl_2$ to provide the required chloride matrix during the leaching stage, instead of other alternatives, *i.e.*, NaCl, $MgCl_2$, was mainly based to the fact that lime is a cheap and efficient reagent for the subsequent metals removal step (Roche *et al.* 1994).

Experimental results regarding the efficiency of metal precipitation with lime are shown in Table 5.25 and Figure 5.13. From the results shown in Table 5.25 it is seen that Pb, Zn and Mn are efficiently removed at pH 9. Increasing precipitation pH to the value of 11, improves the removal of Cd and Mg but the Pb and Zn hydroxides are partially redissolved due to the formation of hydroxocomplexes, *i.e.*, $Pb(OH)^{3-}$, $Zn(OH)^{3-}$, at this alkaline pH.

Table 5.25. Efficiency of metals precipitation from the chloride solutions

Treatment with Lime

pH	Add.$Ca(OH)_2$ g/1000ml	Pb (ppm)	Zn (ppm)	Mg (ppm)	Cd (ppm)	Mn (ppm)
4.4	0	1723	2393	1014	9.95	437
6.0	0.6	1605	2403	1045	9.97	488
6.5	1.1	1175	2163	1072	9.76	463
7.0	2.5	280	783	999	9.39	427
7.5	3.1	61	213	897	9.06	345
8.0	3.6	27.2	27	918	8.77	202
8.5	4.0	15.4	5.63	805	7.55	12.6
9.0	4.5	**13.4**	3.16	541	6.23	**0.8**
10.0	6.1	210	**1.29**	17.6	3.13	0.8
11.0	9.0	167.4	331	**0.8**	3.33	23.9
11.2	14.5	225	817	1.5	**1.34**	41.7

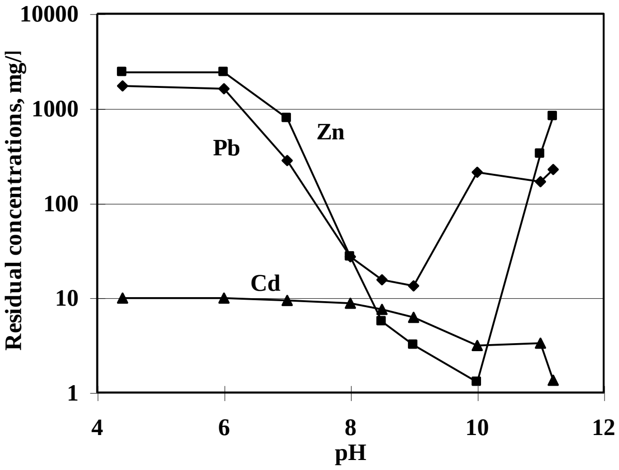


Figure 5.13. *The effect of pH on the removal of metal contaminants from the chloride solution. Precipitation with lime.*

Final polishing of chloride effluent

The solution produced during precipitation contains mainly $CaCl_2$ and can be recycled to the leaching stage in order to maintain the required elevated concentration of chlorides, Cl_{tot}= 4 M. Fresh HCl should be also supplied to compensate for the consumption of acidity during leaching. As a consequence a liquid stream must be discarded to maintain the overall mass balance. This final $CaCl_2$ effluent should meet the environmental regulations for disposal.

The residual concentrations of heavy metals obtained with the addition of lime exceed the environmental limits. A final polishing step is thus required. Precipitation of the residual metals in the form of sulphides, using Ultra-Clear has been tested. Ultra Clear is a commercial product containing sodium dimethyldithiocarbamate and is proposed in the literature (Roche *et al.*, 1994) as a non-toxic, easy to handle alternative to Na_2S with similar advantages, as it leads to the precipitation of highly insoluble sulphides:

$$2\,PbCl_2 + (CH_3)_2NCS_2Na + 2H_2O \rightarrow 2PbS + (CH_3)_2NCO_2Na + 4\,HCl$$

As seen in Table 5.26, this treatment has resulted in reducing the residual concentrations, but the quality of final effluent is not appropriate for disposal in natural receivers, especially for Pb and Cd. Only the criteria for disposal in sewers have been met.

Table 5.26. Removal of residual heavy metal concentrations from chloride solutions with Ultra Clear

pH	Ultra Clear 0.06M (ml)	Pb (ppm)	Zn (ppm)	Mg (ppm)	Cd (ppm)	Mn (ppm)
9.56	0	14.2	3.50	21.9	0.70	0.72
9.49	10	4.7	0.67	20.2	0.65	0.70
9.47	20	4.6	0.92	19.2	0.62	0.69
	30	4.5	1.23	19.0	0.61	0.67
	40	4.5	1.41	17.8	0.59	0.65
	50	4.5	1.68	17.1	0.57	0.63
9.66	60	4.4	1.65	17.1	0.55	0.61
Upper permitted concentrations for disposal						
Natural receivers		0.1	2	/	0.02-0.1	2.0
Sewers		5	20	/	0.5	10

Conceptual flow diagram of the chloride process

The simplified flow diagram of the chloride process is presented in Figure 5.14. It comprises the following treatment steps:

1. Leaching of the contaminated material with a mixture of HCl and $CaCl_2$
2. Removal of metals from the leachate by precipitation with $Ca(OH)_2$
3. Treatment of the final $CaCl_2$ effluent to meet the environmental regulations for disposal.

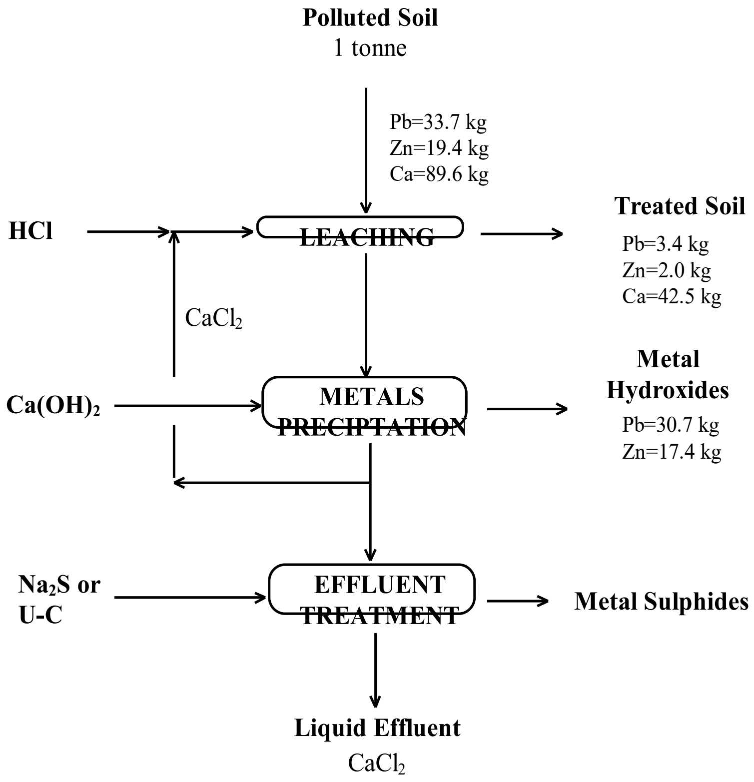


***Figure 5.14**. Schematic flow-diagram of the $CaCl_2$ process.*

5.5 ECONOMIC CONSIDERATIONS

Preliminary mass balance calculations were performed in order to obtain a first estimation regarding (a) reagents consumption and costs and (b) volume of the produced effluents for each one of the above processes. The case examined concerns the treatment of a calcareous material, with the typical composition of oxidic tailings G11 from Lavrion site, *i.e.* Ca 8.6%, Pb 3.4% and Zn 2.0%. All the calculations were based on the removal of metals obtained experimentally, as summarised in Table 5.27.

Table 5.27. Case examined for the comparison of alternative processes.

Material G11, Lavrion. Metals extraction during the leaching tests

	Pb	**Zn**	**Cd**	**Ca**	**Mg**	**Al**	**Fe**	**Mn**
Initial Soil[*], mg/kg	33700	19700	120	85600	13400	15100	56900	3500
	% Extraction							
Citric acid (H_3C) [a] Agitated pulp	66.1	72.8	92	70.9	53.3	12.1	5.5	86
$HCl-CaCl_2$ [b] Column leaching	91.1	91.3	91.8	91.7	93.9	47	7.0	94
Na_2H_2EDTA (Na_2H_2L) [c] Column leaching	88.6	86.7	89.4	77.1	52.6	26.9	36.1	93.2

[*] Mean composition of three samples.

[a] Stirred reactor. Two leaching stages. Amount of reagent: 3.3 moles H_3C/kg soil per stage.

[b] Column test. Total amount of reagent: 6.7 moles HCl/kg soil.

[c] Column test. Total amount of reagent: 4.2 moles Na_2H_2L /kg soil.

The extraction of metals on a molar basis is shown in Fig. 5.15. The total amount extracted during the leaching tests varies between 2.3 to 3.3 kmol/t of soil. More than 60% corresponds to the dissolution of Ca, and only a limited percentage, approximately 14%, is related with the extraction of heavy metals.

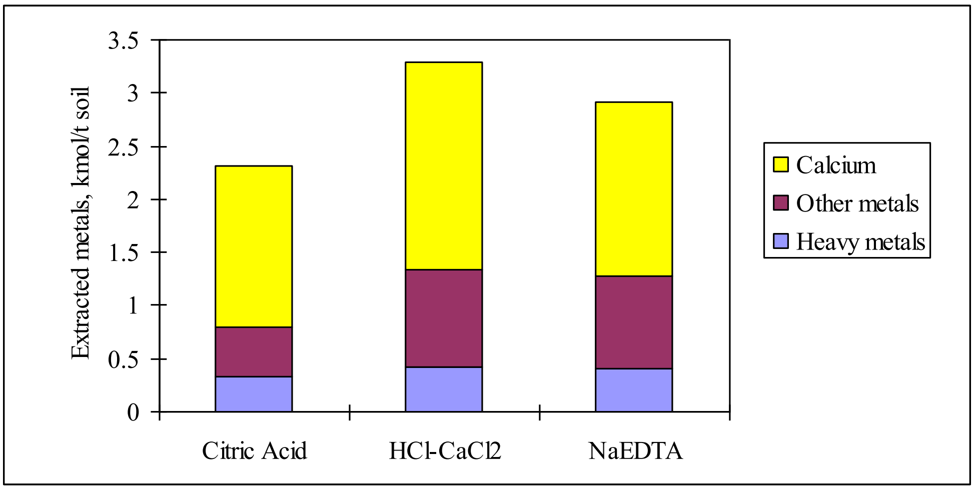


Figure 5.15. *Distribution of extracted metals in the three processes.*

The treatment steps and the stoichiometry of the reactions involved in the three processes are summarised in table 5.28. Lead carbonate, $PbCO_3$, is considered as the typical pollutant to be removed from the soil. Similar equations can be written for the other metal species interfering in the process. The mass balance calculations presented in this section are based on these stoichiometric reactions, taking into consideration the total amount of metals extracted during leaching.

Table 5.28. The stoichiometry of the reactions involved in the three leaching processes

Citric acid process		
Leaching	$\mathrm{H_3C + PbCO_3 = HPbC + CO_2 + H_2O}$	(1)
Metals adsorption	$\mathrm{2HR + HPbC = PbR_2 + H_3C}$	(2)
Resin regeneration	$\mathit{2HCl} + \mathrm{PbR_2 = PbCl_2 + 2HR}$	(3)
Final metals recovery	$\mathit{Ca(OH)_2} + \mathrm{PbCl_2} = \mathbf{Pb(OH)_2} + \mathbf{CaCl_2}$	(4)
	(where C= citrate ligand and R=strongly acidic resin)	
Na_2H_2EDTA process		
Leaching	$\mathrm{Na_2H_2L + PbCO_3 = Na_2PbL + CO_2 + H_2O}$	(5)
Metals precipitation	$\mathit{Na_2S} + \mathrm{Na_2PbL = Na_4L} + \mathbf{PbS}$	(6)
EDTA regeneration	$\mathrm{2HR + Na_4L = 2NaR + Na_2H_2L}$	(7)
Resin regeneration	$\mathit{2HCl} + \mathrm{2NaR = 2HR} + \mathbf{2NaCl}$	(8)
	(where L= EDTA ligand and R=weakly acidic resin)	
HCl-$CaCl_2$ process		
Leaching	$\mathit{2HCl} + \mathrm{PbCO_3 = PbCl_2 + CO_2 + H_2O}$	(9)
Metals precipitation	$\mathit{Ca(OH)_2} + \mathrm{PbCl_2} = \mathbf{Pb(OH)_2} + \mathbf{CaCl_2}$	(10)

Characters in italics denote the reagents and those in bold the effluent streams of the processes.

The stoichiometric requirements of reagents and the amount of solid wastes for the three leaching processes are presented in Table 5.29 and Figure 5.46. It must be underlined that only stoichiometric consumptions are included. Process losses due to solid/liquid separation or washing operations are excluded for the time being.

The estimated cost of reagents for this particular soil sample varies between 22000 and 64000 GRD/t soil. More than 50% of this cost is due to the dissolution of $CaCO_3$, which constitutes approximately 20% in the matrix of material G11. It is pointed out that most of the existing commercial processes, involving the removal of contaminants, have a rather elevated cost. For instance, the cost of Dutch soil washing processes, which are based on the separation of fine particles, ranges between 50 and 200 USD/t depending on the texture of soil material (Trost, 1993, Rulkens *et al.*, 1998).

The total amount of solid wastes was estimated to be 80 and 130 kg/t soil (dry basis) for the citric acid and chloride process respectively. The EDTA process produces a higher amount of solid wastes, *i.e.* approximately 240 kg/t, because extracted Ca is recovered to the solid residue. There are two options for the final disposal of this residue, deposition to a hazardous waste landfill or recycling in the metallurgical industry to recover the metal values, mainly Pb and Zn. Disposal of the solid wastes will increase the overall treatment costs. On the contrary recycling to the metallurgical industry may pay back part of the remediation costs.

Table 5.29. Reagents costs and process effluents for the four leaching processes

STOICHIOMETRIC REQUIREMENTS OF REAGENTS AND RELATED COSTS

	Precipitation	**reagent**	**Acid**		**TOTAL**	**Cost due to Ca diss.**
	kmol/t soil	GRDt soil	kmol/t soil	GRD/t soil	GRD/t soil	GRD/t soil
	$Ca(OH)_2$		*HCl*			
<u>*Citric acid*</u>	0.8 (a)	2850	4.6 (b)	19070	**21920**	*12490*
	Na_2S		*HCl*			
<u>*Na_2H_2EDTA*</u>	2.9 (b)	39740	5.8 (b)	24040	**63780**	*36020*
	$Ca(OH)_2$		*HCl*			
<u>*HCl-$CaCl_2$*</u>	1.3 (a)	4620	6.6 (b)	27360	**31980**	*16280*

(a) Equivalent to extracted metals without Ca	$Ca(OH)_2$:	48 GRD/kg = 3552 GRD/kmol
(b) Equivalent to extracted metals including Ca	Na_2S :	175 GRD/kg = 13704 GRD/kmol
	HCl 33% :	38 GRD/kg = 4145 GRD/kmol

SOLID WASTES TO BE DISPOSED OFF

<u>*Citric acid*</u>	Hydroxides	80 kg/t soil	
<u>*Na_2H_2EDTA*</u>	Sulphides	242 kg/t soil	(120 kg as Ca_2S)
<u>*HCl-$CaCl_2$*</u>	Hydroxides	126 kg/t soil	

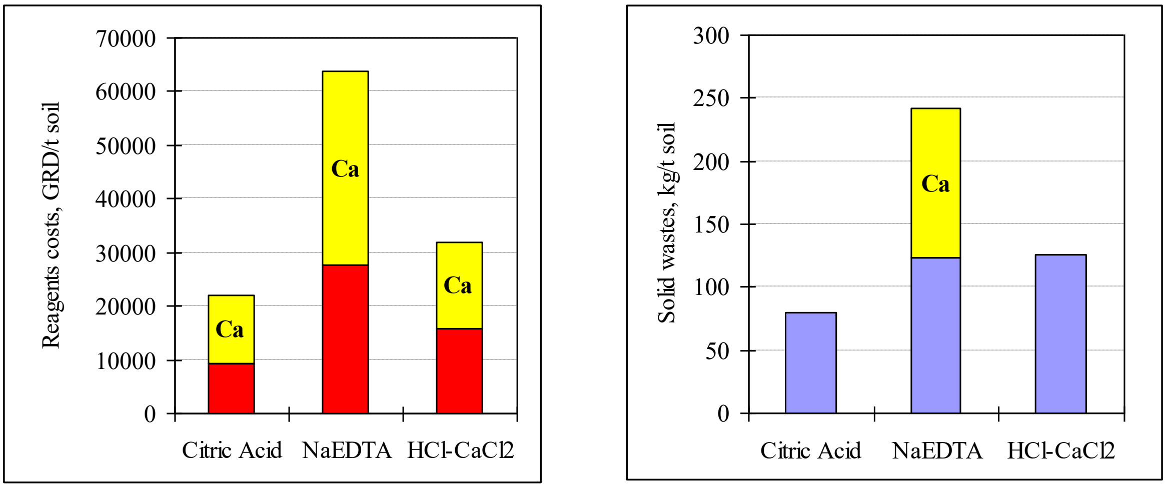


***Figure 5.16**. Estimated cost of reagents and total amount of solid wastes.*

5.6 CONCLUSIONS

The performance of leaching techniques was evaluated on seven samples, representing the *oxidised mineral processing tailings* and the *contaminated soils* of Lavrion. The samples were selected to contain variable levels of contamination, ranging from 35 000 down to 500 mg/kg in Pb.

The selection of leaching reagents was mainly based on the chemistry of Pb, which is the key-contaminant in Lavrion soils. The reagents evaluated during this experimental work were organic acids and chelating agents (*i.e.*, acetic, citric acid, EDTA) and an acidic brine consisting of $CaCl_2$ and HCl.

Small scale experiments, using *test tubes*, were carried out as an initial screening procedure in order to evaluate the performance of citric acid, EDTA and $CaCl_2$-HCl. The parameters, which were investigated with this experimental technique included: a) level of soil contamination, b) concentration of reagents in the aqueous solution and c) solid to liquid ratio.

The extraction rates were found to vary considerably for the different soil samples, without a clear trend regarding the level of contamination. The maximum removal of metals was achieved using the acidic brine, $CaCl_2$-HCl, with average extraction rates 86% for Pb, 93% for Zn and 77% for Cd.

High concentration levels and low pulp densities were found to be required in order to maximise the removal of contaminants from soils.

The experiments in *agitated reactors* were carried out on a heavily contaminated waste material, containing 3.4% Pb. The leaching agents which were tested include : acetic acid 1M, oxalic acid 0.5M, citric acid 0.33 M and Na_2EDTA 0.25 M. The kinetics of leaching reactions was also studied during the experimental work in agitated reactors.

From the results it was found that *oxalic acid* is ineffective for the removal of heavy metals. *Acetic acid* can achieve reasonable extractions of Zn, 64%, and Cd, 100%, but the extraction of Pb is limited 46% and the residue remains toxic with respect to this metal. Lead removal with *citric acid* and *Na_2EDTA* reached a level of 66% and 80% respectively. The residual soil for these two reagents was characterised as non-toxic.

Regarding kinetics, it was found that the major part of Pb is removed within the first hour of leaching. The incremental removal is minimal afterwards especially for the EDTA and the acetic acid systems. A second treatment with fresh leaching solution was found to improve slightly the removal.

From the results obtained in test tubes and agitated reactors, it was concluded that the most efficient leaching systems are the strong chelator Na_2-EDTA and the acidic chloride brine HCl-$CaCl_2$. These leaching reagents were used for the *column experiments*, which were applied on two samples containing 3.4 and 2.4 % Pb.

Evaluating the results obtained with the two leaching systems the following conclusions were drawn.

1. Both leaching systems can achieve very high removal rates for Pb, Zn and Cd exceeding 87%.
2. Best results were obtained with the acidic brine $CaCl_2$-HCl, with extraction rates up to 97% for Pb, Zn and Cd.

3. Treatment with $CaCl_2$-HCl can even reduce the concentrations of the above heavy metals below the international standards for industrial use of land. In order to obtain such low residual concentrations a high excess of HCl is required.
4. Despite the strong chelating capabilities of Na_2EDTA it was not possible to obtain such low residual concentrations. This suggest that some species of Pb, Zn, and Cd are refractory to chelation and can be dissolved only under strongly acidic conditions.
5. Arsenic is extremely immobile at least with the leaching systems tested during this experimental work.
6. Both leaching systems attack the soil matrix and result in the dissolution of important metal components, such as Mn, Ca and Mg. This result in a substantial weigt loss ranging between 44 and 49 % for Na_2EDTA and 17 and 38 % for $CaCl_2$-HCl.

For the development of Integrated Leach Processes, several alternative flowsheets were evaluated, focusing to the production of environmentally compatible effluents and the minimisation of reagents costs.

Processes based on the use of Organic Acids

For the leaching systems which are based on the use of organic acids and chelators, it was thought more appropriate to investigate process flowsheets comprising *complete regeneration and recycling* of the leaching solution. Two alternative flowsheets were investigated experimentally: a) the first comprises a resin treatment step for the removal of metals from the leachate and the simultaneous regeneration of the organic reagent, b) the second is based on the precipitation of metals as hydroxides or sulphides (with $Ca(OH)_2$, NaOH or Na_2S) and the subsequent regeneration of the reagent.

The use of *strongly acidic cationic resins* for the removal of metals from the citric acid leach solutions seems to be a promising alternative, as it gives metal removal rates near 100%. Moreover, the product is a regenerated acid solution that can be recycled directly to the leaching stage. Additional treatment stages are however required in order to recover the metals and regenerate the resin. This cation exchange treatment was found to be completely inefficient for the Na_2EDTA leach solution.

Regarding *precipitation techniques* applied on the organic leach solutions the following conclusions were drawn:

Precipitation with NaOH was inefficient for the *citric acid* solution, while $Ca(OH)_2$ was found to remove the metals efficiently. For Na_2-EDTA, a two step precipitation technique seems to be more appropriate: addition of NaOH for the coprecipitation of iron and arsenic, followed by the addition of Na_2S for the precipitation of heavy metals.

Regeneration of the solution following the precipitation step was also tested for the Na_2H_2EDTA process. The results show that a weekly acidic resin can regenerate the initial acidity by adsorbing the excess Na^+ ions, which are introduced in the solution during precipitation.

The Chloride process:

Total recycling is not possible for the HCl-$CaCl_2$ system. Fresh HCl should be supplied to compensate the consumption of acidity and a liquid stream must be discarded to maintain the mass balance. This bleed stream should satisfy the environmental regulations for disposal.

The major part of the metals is recovered from the leach solution by precipitation with lime. It was found that the residual concentrations obtained from the lime treatment do not satisfy the environmental regulations for disposal. A final polishing step with the application of Ultra-Clear, involving precipitation of sulphides, has reduced the residual concentrations, but the quality of final effluent was still not appropriate for disposal in natural receivers, especially for Pb and Cd. Only the criteria for disposal in sewers have been met.

A preliminary cost analysis was also carried out in order to evaluate the cost effectiveness of the processes. Reported treatment costs for commercial soil washing processes range between 50 and 200 USD/t soil, with most important cost factor the content of the soil in fine particles. Cost calculations for the leaching processes were conducted considering as base case the treatment of a calcareous material, with the typical composition of oxidic tailings G11 from Lavrion site, *i.e.*, Ca 8.6%, Pb 3.4% and Zn 2.0%. The estimated cost of reagents for this particular soil sample varies between 22,000 and 64,000 GRD/t soil. More than 50% of this cost is due to the dissolution of $CaCO_3$, which constitutes approximately 20% in the matrix of this material.

For calcareous soils, which are typical in the site of Lavrion, it is essential to identify alternative chelators, which could remove selectively the heavy metals without dissolving the $CaCO_3$ matrix. The reagents investigated during this experimental work could led to cost effective processes, mainly for soils poor in calcite. The most promising amongst them is the $CaCl_2$-HCl mixture, which can achieve very high extraction rates and it is based on the use of low cost reagents.

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SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION

LIFE Project, Contract No.: 93/GR/A/4/GR/4567

VOLUME 3

ENVIRONMENTAL CHARACTERISATION OF LAVRION SITE – DEVELOPMENT OF REMEDIATION TECHNIQUES

CHAPTER 6

CONCLUSIONS

ATHENS, DECEMBER 1999

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6. CONCLUSIONS

The activities undertaken by NTUA in the framework of this project, include the followings:

- Identification and detailed characterisation of the various categories of wastes in Lavrion area and characterisation of contaminated soils, in order to select the appropriate remedial technology for each category of material.
- Evaluation of alternative technologies for the rehabilitation of sulphidic tailings and demo scale application of three techniques on Kavodokanos pyrites.
- Investigation of chemical stabilisation techniques for the remediation of carbonaceous tailings and soils and demo-scale application on Savoura tailings.
- Evaluation of chemical leaching techniques for the removal of contaminants from carbonaceous tailings and soils, development and evaluation of integrated processes.

Environmental characterisation of the site

The intensive mining and metallurgical activities in Lavrion have resulted in the formation of huge spoils of wastes, containing variable amounts of heavy and toxic metals and contributing to the widespread contamination of soil, surface and ground waters. The spoils identified in the area were classified into three main categories, *sulphides*, *carbonates* and *slags*, exhibiting different geochemical and environmental characteristics.

The s*ulphides* are flotation tailings rich in pyrites. They are contained in four main stockpiles around the Metallurgical plant and at Thoricos bay and their volume was estimated to approximately 1,200,000 tons. The sulphide minerals contained in the spoils are naturally oxidised under the action of meteoric water and atmospheric oxygen and this result in the generation of acidic and highly contaminated waters. Run off and seepage waters accumulated in the vicinity of pyrites were found to be very acidic and with high concentrations of dissolved toxic elements, e.g., pH 1.9, Pb 1.7 ppm, Zn 1150 ppm, As 800 ppm. Due to their partial oxidation, they also contain an appreciable amount of bioavailable metals and they are characterised as toxic following the TCLP test. The main environmental risks related with their presence in Lavrion area is the generation of acidic contaminated waters, which transfer the contamination to the adjacent soils, and air transfer of contaminated particles, which are inhaled by humans or deposited in the soils.

The *carbonates* are beneficiation tailings rich in carbonate minerals. They are found in two main stockpiles all along the west site of Lavrion city and at Thoricos bay and their amount was estimated to more than 7,000,000 tons. They contain very high levels of total and bioavailable metals, e.g. up to 35,000 ppm total and 12,000 ppm bioavailable Pb. Following the TCLP test, they are characterised as highly toxic, with leachable Pb up to 230 mg/L when the corresponding limit is 5 mg/L. They occupy an extended area, where public, residential and agricultural activities have been developed. Grapes and olives cultivated on the top of theses tailings were found to accumulate high levels of Pb, exceeding guidelines by 2 or 10 times respectively. Risks emanating from these spoils include direct contact of humans with the contaminated material, inhalation or ingestion of airborne contaminated particles and consumption of locally grown vegetables and fruits.

The third category of wastes, *slags*, are the residue of the lead smelting operations, with a siliceous matrix and an estimated volume of more than 5,000,000 t. Slags have been considered in the past as inactive and safe for the environment. The present study has showed that partial dissolution of toxic metals could take place, when the big slag pieces are ground to fine particles. However, slags are evaluated as less hazardous, compared to the rest tailings of Lavrion. Due to their coarse texture and their hard vitreous matrix, they have infinite water permeability and are not susceptible to wind erosion. Risks for water or air transfer of contaminants were therefore estimated as minimal.

Natural processes and anthropogenic activities have resulted in the widespread contamination of soils. Based on the *total* concentration of contaminants, the primary metals of concern at Lavrion surface soils are *As* followed by *Pb* and to a lesser extent *Cd* and *Zn*. Arsenic was seen to be quite immobile with all the alternative leaching tests, which were applied to evaluate the mobility and availability of elements. On the contrary Pb was found to be highly leachable. More than 75% of the area examined contains Pb, which is leachable in EDTA at values exceeding the Netherlands Intervention standards (530 mg/kg) and 25% is characterised as toxic following the TCLP procedure. Phytoaccumulation in grapes and olives was found to exceed the guidelines for edible products, even in soils with relatively low contamination. The major risks for humans are similar to that prevailing for the carbonate tailings and include the direct contact, ingestion and inhalation of contaminated particles and the introduction of contaminants to the food chain.

Considering the particular characteristics of the wastes and soils and the specific environmental risks associated with each type of material, three category of techniques were investigated: the *isolation* techniques were considered to be more suitable for eliminating the risks associated with the sulphidic tailings, while *chemical immobilisation* and *removal of metals* were evaluated for the treatment of oxidic tailings and soils.

Acid Drainage Control – Rehabilitation of sulphidic tailings

The risk assessment study for the case of sulphidic tailings showed that the remediation scheme should aim at the reduction of acid generation potential and the elimination of wind erosion and dusting. Three rehabilitation options, including two dry covers and addition of alkalinity, were evaluated on a demonstration scale on Kavodokanos pyrites. This stockpile of pyrites covers an area of 40000 m^2 and contains approximately 600000 t of high sulphur content tailings. The three options were developed on an area of 2500 m^2, which was divided in 4 equal quadrants. One quadrant served as the control plot and the other three hosted the alternative remedial options. The first dry cover was constructed using a synthetic liner (HDPE) as oxygen and water barrier. The second cover involved the use of a compacted clay layer. The third solution involved the addition of limestone at an amount of 20% of the stoichiometric requirement. The objective of this technique was to promote the oxidation-neutralisation reactions around the pyrite particles in order to create an impermeable layer ("hard pan") from the secondary neutralisation products.

After a two year monitoring period the following conclusions were drawn. The amount of water, which percolates through Kavodokanos pyrites if no action is taken (control area), corresponds to approximately 210m^3 per hectare per year. This water is very acidic, pH=1.2, and contains a very high load of metal contaminants, e.g., Fe 40 g/L, Zn 15 g/L, Mn 5.9 g/L, As 745 mg/L, and Cd 58 mg/L. Part of this contamination is released as seepage to the surrounding soils.

The two covers, based on the use of HDPE geomembrane and a compacted clay layer respectively, were both found to provide an efficient barrier to the infiltration of rainwater, suppressing thus the production of acidic waters and the migration of contaminants. The

HDPE cover has effectively inhibited the percolation of water into the material and no leachate was collected from this plot. The water collected in the lysimeter of the clay cover corresponds to approximately 5% of the drainage volume produced in the control area and it is probably due to the dehydration of the clay layer during the dry summer period. The integrity of the clay layer has been reestablished after the first rainfalls in autumn. Finally the addition of limestone in the fourth plot has initially increased the permeability of the material and the cumulative volume of infiltrated water corresponding to the first 2 years was increased.

The most expensive technique is the geomembrane cover, estimated to 4,400 GRD/m^2 for an HDPE sheet of 2 mm. Using a thinner sheet of 1mm, the cost is reduced to 3,100 GRD/m^2. The cover incorporating compacted clay as the barrier layer had a cost of 2,800 GRD/m^2. The major disadvantage of the HDPE cover, in addition to its relatively high cost, is the uncertainty about the long term performance of the geomembrane sheet. This thin synthetic material can be subjected to several irreversible damages through mechanical penetration and chemical degradation processes. On the contrary the compacted clay option is based on the use of a natural material with known properties and predictable behaviour. The most crucial issue for its good performance under the dry climatic conditions of Lavrion is the efficient protection of its moisture, which can be achieved optimising the upper protective layers.

The limestone addition is a low cost option, which can be efficient when applied at a rate stoichiometrically equivalent to the acid generation capacity of the spoils. Substoichiometric addition of limestone to high grade pyrites has not resulted in the expected formation of hardpan during the two years monitoring period. Research is currently in progress to optimise the technique and enhance the mechanism of hardpan formation.

Chemical stabilisation techniques

Stabilisation methods aim at transforming the contaminants to low solubility and low availability forms. They involve mixing of the contaminated soil material in situ with appropriate substances and curing from some time in order for the reactions to proceed. They were investigated as a low cost remedial option, for the carbonaceous tailings and soils of Lavrion, where the metal contaminants occur in highly bioavailable species. The risk assessed for both the carbonaceous tailings and soils is high and it is associated with inhalation of wind blown dust and also with the bioaccumulation of heavy metals in the plants, which are entering in the food chain.

The efficiency of stabilisation techniques was tested on the oxidic tailings "Savoura". This material is considered as hazardous because of the elevated concentration of heavy metals and the high bioavailable-phytotoxic fraction of heavy metals. It is also characterised as toxic according to the EPA TCLP test. Several inorganic and organic wastes and law cost materials were tested as stabilising agents. The effect of these additives was evaluated with chemical and biological tests.

Best results were obtained using *phosphates*, *fly ash* and *biological sludge*. These additives were successful in reducing the leachability of Pb and Cd, below the regulatory TCLP limits at relatively low doses, i.e., less than 1% for phosphates and 10% for fly ash and biological sludge. The evaluation of phytoavailability by applying EDTA and DTPA tests has also indicated a 50% decrease in the solubility of contaminants.

Despite the reduction of heavy metals solubility, the stabilisation treatment was not able to reduce the actual uptake of toxic elements in the plant tissues, as estimated from the cultivation of *Phaseolus Vulgaris* species on the stabilised soils. The concentrations of Pb, Zn, Cd and As accumulated in the leaves remain very high compared to the normal range encountered in the leaves of plants. Risks for humans through food intake are not attenuated with this treatment, it is thus essential to avoid the cultivation of edible plants on this soil material. On the contrary, the development of a vegetative cover using nonedible plant species could be highly beneficial, suppressing dusting and reducing the risks for the inhalation of airborne contaminated particles.

Concerning the effect of additives on the growth of plants it was found that both phosphates and fly ash had a negative effect while the organic rich materials, such as biological sludge and compost, showed a rather positive effect on the production of phytomass.

Additional laboratory experiments were conducted using mixtures of the successful inorganic and organic stabilisers in order to combine their action, reducing the solubility of all the metals and providing the appropriate substrate for phytomass production. Based on the results obtained, a remediation scheme was proposed including treatment of the soil with mixture of stabilising agents to immobilise heavy metals and application of a vegetative cover, aiming at suppressing wind erosion.

Field tests were conducted on Savoura tailings, at location Neraki, in order to evaluate the effectiveness of this scheme under the conditions prevailing on site. The field test area, approximately 1000m^2, was divided into six (6) equal test pads. The stabilising agents added in each test pad are: compost and phosphates, fly ash and compost, fly ash and biological sludge, phosphates and biological sludge, and finally biological sludge. Furthermore, a control test pad was constructed in order to evaluate the effectiveness of the stabilisation. A sprinkling system was installed and irrigation was applied for one month after the application of the stabilising agents in order to promote the stabilisation reactions. The pilot area was sown with a mixture of seeds, consisting of several yearly and perennial plants.

The addition of stabilisers has reduced the solubility of Pb, Zn, and Cd by a factor ranging between 60 and 95%, and the stabilised material was characterised as non-toxic according to the TCLP test. Stabilisation was also found to be an indispensable pretreatment stage to support the development of vegetation, as a final protective cover suppressing the generation of dust. The five plots, where the soil was treated with the addition of stabilising agents, were covered with dense vegetation, which was successfully reproduced during the second growing period. Very few and poorly developed plants appeared in the control plot during the first year, but vegetation was not sustained and the area remained completely bare during the second year.

The cost of stabilisation, as applied in Lavrion field tests, was found to range between 5000 and 9700 GRD/m^2, with most important cost factor the transfer of stabilising materials to the remediation site. Considerable cost savings could be achieved using locally produced wastes and by-products. For instance, using biological sludge from Lavrion wastewater plant could reduce the costs in the range 1500 to 6000 GDR/m^2.

Removal of contaminants – Leaching techniques

Removal of contaminants can provide a permanent solution to the environmental problem. This category of technologies includes all the processes capable of removing the pollutants from the soil matrix with the use of physical mineral processing techniques or leaching techniques. The application of leaching methods was investigated in the framework of this project for the removal of heavy metals from the carbonaceous tailings and soils of Lavrion.

Several leaching reagents were tested, such as oxalic acid, acetic acid, citric acid, EDTA and an acidic chloride solution. Oxalic acid was found to be inefficient for the removal of heavy metals. Acetic acid and citric acid were able to remove 46 and 66% of Pb, respectively, from a heavily contaminated waste material containing 3.4% Pb. Removal rates higher than 80% were obtained using the di-sodium EDTA salt and HCl-$CaCl_2$ solutions.

Leaching techniques can be applied either in situ or by excavation and leaching on site, in heaps or using reactors. Column experiments, simulating the in situ or heap leaching techniques, were carried out using the most successful leaching reagents, i.e. the EDTA and HCl-$CaCl_2$ solutions. Column tests confirmed that both leaching systems can achieve very high removal rates for Pb, Zn and Cd exceeding 87%. Best results were obtained using the acidic brine $CaCl_2$-HCl, which can even reduce the concentrations of the above heavy metals near the international standards for industrial use of land. An undesirable side effect, observed for both leaching reagents, is the co-dissolution of important soil components and more particularly $CaCO_3$.

For the development of integrated processes all the subsequent treatment stages were studied, including the metal removal from the pregnant solution, the regeneration of the reagents and the final polishing of liquid effluents to meet environmental discharge regulations. *Resin treatment* and *precipitation techniques* were mainly investigated for the subsequent treatment stages. Based on the experimental results, several alternative flowsheets were evaluated, focusing to the production of environmentally compatible effluents and the minimisation of reagents costs.

The use of *strongly acidic cationic resins* seems to be a promising alternative for the removal of metals from the Citric Acid leach solutions, as it gives metal removal rates near 100%. Moreover the product is a regenerated acid solution that can be recycled directly to the leaching stage. For the Na_2H_2EDTA process, *a two step precipitation technique* seems to be more appropriate: addition of NaOH for the coprecipitation of iron and arsenic, followed by the addition of Na_2S for the removal of heavy metals. Regeneration of the solution following the precipitation step was also tested for Na_2H_2EDTA. The results show that a weekly acidic resin can partially regenerate the initial acidity by adsorbing the excess Na^+ ions, which are introduced in the solution during precipitation. Precipitation with $Ca(OH)_2$ was tested for the removal of metals from the acidic $CaCl_2$ solution. Maximum removal was obtained at pH=9, but residual concentrations do not satisfy the environmental regulations for disposal. Precipitation of residual metal contaminants in the form of sulphides was investigated as a final polishing step. Following this treatment, the effluent satisfies existing criteria for disposal in sewers.

A preliminary cost analysis was also carried out in order to evaluate the cost effectiveness of the processes and their competitive position towards other soil remediation alternatives. Reported treatment costs for commercial soil washing processes range between 50 and 200 USD/t soil, with most important cost factor the content of the soil in fine particles. For the leaching processes, which were investigated in this project, the crucial cost factor was found to be the calcite content of the soil. For a soil containing approximately 20% of $CaCO_3$ in its matrix, the cost of reagents was estimated to vary between 22,000 and 64,000 GRD/t soil, depending on the process, and more than 50% of this cost is due to the dissolution of $CaCO_3$. The above estimated *reagents costs* are within the cost range of existing commercial processes, but it is pointed out that they represent only part of the total treatment costs.

Leaching techniques are obviously an expensive treatment option particularly for soils rich in calcite, which are typical in the site of Lavrion. Further research is required to improve their performance and reduce the application costs to levels, which could be attractive for large scale remediation projects.

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APPENDIX

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Appendix A

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Appendix A1

International standards for the quality of Soils

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Soil Quality Standards

Table A1

Netherlands Standards for soils

Contaminant	Target Value	Intervention Value
	(ppm, µg/g)	
Pb	85	530
Zn	140	720
Cd	0.8	12
Cu	36	190
As	29	55
Cr	100	380
Ni	35	210
Hg	0.3	10
Ba	200	625
Co	20	240
Mo	10	200

Table A2

Canadian Standards for soils

Contaminant	Land Use			
	Agricultural	Residential/ Parkland	Commercial	Industrial
	(ppm, µg/g)			
Pb	70	140	260	600
Zn	200	200	360	360
Cd	1.4	10	22	22
Cu	63	63	91	91
As	12	12	12	12
Cr_{total}	64	64	87	87
$Cr_{(VI)}$	0.4	0.4	1.4	1.4
Va	130	130	130	130
Ni	50	50	50	50
Hg	6.6	6.6	24	24
Ba	750	500	2000	2000

Wastes Toxicity Limits

Table A3

EPA, TCLP toxicity limits

Contaminant	(ppm)
Pb	5
Cd	1
As	5
Cr	5
Hg	0.3

Water Standards

Table A4

Contaminant	Effluent Quality (Saronikos, FEK 1132/79)
Pb	0.1
Zn	1.0
Cd	0.1
Fe	2.0
As	0.5
Cr	2.0
Hg	0.005
Ba	20

Appendix A2

Detailed data for the depth of contamination

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Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Bodosakis (close to the road) **G1**	(0-0.8)	58000	1700	20	44000	31.86	0.9	27.1	0.04	
	(0.8-1.30)	16000	7600	70	21000	26.82	2.1	22.8	0.17	
	(1.30-1.6)	7000	21300	10	8000	16.52	3.8	18.6	0.51	
	(1.6-2.6)	15000	71700	20	2000	2.08	10.3	25.2	1.12	
	(2.6-3.0)	20000	84400	20	2000	1.72	10.4	24.3	1.44	
	(3.0-3.9)	18000	77600	35	2000	2.55	9.8	25.4	1.55	
	(3.9-4.3)	12000	45600	5.5	2000	1.1	12.4	21	1.2	

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Bodosakis (Close to the sea) **G2**	(0-0.8)									
	(0.8-1.3)	9000	1400	0	32000	33.31	1.8	26.8	0.14	
	(1.3-2.3)	11000	1500	20	30000	30.86	2.1	26	0.1	
	(2.3-2.8)	16000	9500	6.5	4000	18.84	4.4	19.5	0.35	
	(2.8-3.4)	39000	15000	55	6000	11.62	6.4	19	0.28	
	(3.4-4.5)	8000	29200	55	2000	8.28	12.3	19.5	0.51	
	(4.5-5.0)	16000	15500	100	4000	1.95	13.9	9	0.92	

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Tailings Pond (South part) **G3**	(0-2.5)	3000	4800	25	4000	3.5	13.9	10.6	1.1	
	(2.5-3.9)	7000	7900	35	4000	3.65	13.1	11.7	1.18	
	(3.9-4.9)	34000	46600	300	27000	4.6	5.9	15.7	0.6	
	(4.9-6.0)	2400	47900	90	500	2.88	5.5	3.3	1.34	52.1
	(6.0-6.6)	1800	51600	200	500	2.74	6.1	3.4	3.84	50.2

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Tailings Pond (North part) **G4**	(0-0.48)	4000	2800	25	500	7.6	5	18.9	1.5	
	(0.48-0.78)	2000	7200	50	500	8.14	4.8	16.3	1.83	
	(0.78-1.90)	2600	4500	30	500	7.7	5.2	18.7	1.43	28.5
	(1.90-2.70)	2000	3900	30	2000	3.26	17.2	11.1	0.96	
	(2.70-3.80)	3000	4300	40	2000	3.26	14	11.9	1.28	
	(3.8.-4.30)	3000	4300	35	500	2.68	11.6	11.5	1.66	
	(4.30-4.75)	7000	7500	40	2000	2.29	12.5	11.7	1.54	
	(4.75-5.00)	8000	52700	20	4000	5.96	6.8	8	1.19	
	(5.00-5.80)	3000	83800	30	500	4.53	6.6	3.9	1.08	
	(5.80-6.50)	1000	86300	20	500	4.13	5.9	2.6	1.2	
	(6.50-7.50)	1000	64700	20	500	3.3	5.2	3.2	1.3	
	(7.50-7.80)	1000	78300	20	500	5.9	9.3	4.6	1	

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Thorikos Beach (close to the sea) **G5**	(0.00-1.90)	600				0			4.18	
	(1.90-2.50)	2000				2.855			3.915	
	(2.50-3.70)	3400				5.71			3.65	
	(3.70-4.30)	5100				7.585			2.525	
	(4.30-5.20)	6800				9.46			1.4	
	(5.20-6.50)	7400				14.72			0.98	

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Kavodokanos (North heap) **G6**	(0.0-1.00)	11000	29300	100	6000	5.2	12.7	13.6	1.05	
	(1.00-1.70)	6000	7400	30	6000	8.43	12.6	15.7	0.82	
	(1.70-2.40)	5500	8800	40	6000	8.37	12.9	15.4	0.81	
	(2.40-3.70)	5000	10200	50	6000	8.31	13.2	15.1	0.8	
	(3.70-4.30)	5500	9100	42.5	7000	9.375	13.1	15.85	0.72	
	(4.3-6.3)	6000	8000	35	8000	10.44	13	16.6	0.64	
	(6.30-7.00)	4050	6950	47.5	4000	10.045	13.95	13.25	0.91	
	(7.00-7.40)	2100	5900	60	0	9.65	14.9	9.9	1.18	16.2
	(7.40-8.20)	400							0.56	
	(8.20-9.50)	300							0.94	

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Kavodokanos (South heap) **G7**	(0-0.4)	5000	28900	100	3000	8.63	6.6	13.9	2.58	29.5
	(0.4-1)	400	83400	90	500	8.6	10.3	9.7	1.62	13.2
	(1.0-1.2)	200	40900	70	500	8.58	12.3	11.4	1.61	15.4
	(1.2-1.6)	1000	34700	60	500	6.57	12.2	11.9	1.96	19
	(1.6-2.5)	3400	12000	55	1000	2.18	13.4	6.9	1.59	28.9
	(2.5-2.9)	2000	7200	50	1000	1.4	12.3	5.7	2.29	31.7
	(2.9-3.5)	800	150000	45	500	0.28	9.3	3.8	4.76	49.4
	(3.5-3.9)	300	200	55	500	0.246	8	2.8	7.88	54.5
	(3.9-4)	300	300	53	500	0	7.5	2.85	0.94	54.8
	(4-4.6)	400	400	50	500	0.44	7	2.9	9.52	55.1
	(4.6-5)	300	300	45	500	0.26	7.2	2.9	9.86	55.3
	(5-5.5)	300				0			7.09	
	(5.5-6)	200				0			6.14	
	(6-6.2)	200				0			6.14	
	(6.2-6.4)	400				0			7.1	
	(6.4-7.1)	200				0			0.96	
	(7.1-8)	300				0			1.56	
	(8-8.2)	400				0			0.82	

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Wash. Circuit Tailings (NW heap) **G8**	(0-1.10)	20400	14400	120	2400		9.6	3.56		54.72
	(1.10-1.70)									
	(1.70-13.1)	20160	20100	148	1600		10.4	3.61		52.1
	(13.7-15.0)	2760	2650	32	400		12.4	2.66		52.06

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Washing Circuit Tailings (middle heap) **G9**	(0-1.4)	24300	18600	130	3000	0	12.74	7.01		
	(1.4-5.2)	24300	18600	130	3000	0.27	12.74	7.01		
	(5.2-5.8)	24300	19250	135	3000		11.9	6.88		
	(5.8-7.5)	24300	19900	140	3000	0	11.06	6.75		
	(7.5-8.1)	14650	12000	100	1750		11.50	5.265		
	(8.1-8.25)	5000	4100	60	500		11.95	3.78		
	(8.25-8.75)	1000	1200	30	500		18.41	2.39		
	(8.75-9.1)	0	240	20	500		14.55	2.96		
	(9.1-9.3)	3100	810	20	1000		6.8	4.54		
	(9.3-10)	400	440	0	1000		4.39	3.52		

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Washing Circuit Tailings (south heap) **G10**	(0-8.5)	21300	31100	300	400		25.82	2.43		21.46
	(8.50-9.00)				800					
	(9.00-10.70)	19600	31900	260	800		25.94	2.61		23.62
	(10.70-12.30)	21000	33700	260	1200		21.94	2.78		27.4
	(12.30-13.70)	21800	32800	250	400		22.59	2.97		26.22
	(13.70-14.60)	8700	7700	68	<400		8.48	3.33		56.78
	(14.60-15.40)	2400	7200	36	<400		17.08	2.74		37.2

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
French Company Washing Tailings **G11**	(0-1)	37000	23200	130	3000	0	6.64	5.94	2.68	45.44
	(1-1,6)									
	(1,6-3,2)	37000	23600	120	6000	0.34	8.32	6.48	2.9	37.76
	(3,2-3,8)									
	(3,8-5,5)	700	530	12	400	0.25	7.08	1.44	0.81	69.48
	(5,5-6,7)	1500	1130	12	400		8.25	3.36	2.06	60.52

Sample		CONTAMINANTS, ppm					OTHER, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Thorikos Beach (close to the road) **G12**	(0.00-4.00)	8560	75800	310	4000	10.24	5.32	16.64	0.7	6.04
	(4.00-5.30)	26800	170600	820	5000	3.77	8.64	11.51	0.98	6.8
	(5.30-7.10)	26800	160000	850	4000	4.1	8.96	9.33	1.14	7.02
	(7.10-8.00)	42800	172400	680	11000		6.3	13.42	1.04	5.44
	(8.00-10.0)	1400	2400	16	400		6.87	1.77	0.84	70.24

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G13**	(0-0.40)	8500	21300	170	3000		3.17	3.84	3	
	(0.40-1.00)									
	(1.00-3.20)	8300	16200	130	2000		4.88	3.33	3.4	
	(3.20-5.30)	8300	4300	80	<1000		6.3	2.28	2.7	
	(5.30-7.85)	<200	1400	70	<1000		4.92	3.11	4.5	
	(7.85-10.00)	300	2700	80	<1000		21.18	3.77	3.9	
	(10.00-1.00)	700	1700	70	<1000		7.89	2.19	2.7	
	(11.00-2.30)	600	1600	70	<1000		8.64	2.1	2.1	
	(12.30-2.60)	600	2000	70	<1000		5.18	2.84	2.2	
	(12.60-4.50)	<200	1700	70	<1000		2.25	2.99	4.1	
	(14.50-5.30)	600	2600	70	<1000		3.1	4.45	4.8	
	(15.30-7.20)	<200	1100	60	<1000		2.65	5.88	7	

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G14**	(0-0.60)	10600	10200	68	1600		20.47	4.03		19.86
	(0.60-1.00)									
	(1.00-1.45)	19000	14900	72	2800		13.02	4.84		36.04
	(1.45-1.80)	40000	38600	20	<400		12.58	8.53		33.94
	(1.80-2.50)	3600	2000	<20	<400		4.79	2.17		73.18
	(2.50-3.50)	600	400	<20	<400		5.16	1.44		
	(3.50-4.50)	200	400	<20	<400		0.9	3.2		
	(4.50-5.30)	2700	2700	20	<400		12.62	2.8		
	(5.30-6.20)	<200	170	<20	<400		27	1.02		
	(6.20-7.00)	<200	100	<20	<400		21.78	2.15		29.08

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)		Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G15**	(0-0.40)	8200							3	49.36
	(0.40-2.50)								3.1	
	(2.50-4.30)	500							0.3	34.4

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)		Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G16**	(0-0.70)	40000	35700	100	1600		4.28	7.2		
	(0.70-1.00)	33200	35100	100	1200		5.55	8.8		
	(1.00-4.00)	23000	27800	28	800		9.44	14.8		
	(4.00-5.00)	400	1000	<20	<400		12.02	4.8		
	(5.00-5.30)	<400	170	<20	<400		10	4.4		48.94

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
G17	(0-0.37)	3200	2400	40	500		7.3	3.43		
	(0.37-0.58)	250	250	30	<500		14.08	2.75		
	(0.58-1.28)	<250	230	<20	<500		12.9	2.33		
	(1.28-4.60)	<250	260	30	<500		12.82	3.92		
	(4.60-5.30)	<250	210	20	<500		7.68	4.05		

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G18**	(0-0.40)	4800	3500	<20	400		0.36	4.28		71.1
	(0.40-1.00)	600	800	<20	<400		20.84	2.05		30.48
	(1.00-1.40)	200	200	<20	<400		24.17	1.61		24.4
	(1.40-2.80)	1200	1200	<20	<400		27.6	1.77		18.5
	(2.80-3.26)	400	1000	<20	<400		24.4	1.8		23.84
	(3.26-5.30)	500	900	<20	<400		25.2	1.94		26.68

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)		Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G19**	(0-0.40)	30000	26400	200	3600		8.68	6.4		
	(0.40-1.00)									
	(1.00-1.30)	26800	21900	100	5200		8.62	6.4		
	(1.30-1.60)	22200	18700	100	2800		8.54	5.2		
	(1.60-2.48)	11600	8300	48	<400		5.69	3.66		
	(2.48-4.00)	500	500	<20	<400		7.84	3.52		
	(4.00-5.00)	200	280	<20	<400		13.55	1.66		
	(5.00-6.00)	500	600	<20	<400		7.08	3.98		

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G21**	(0-0.30)	500	700	<20	<400		10.31	3.72		54.32
	(0.30-0.50)	400	500	<20	<400		7.82	3.9		60.32
	(0.50-0.84)	400	900	<20	<400		12.22	3.44		47.32
	(0.84-1.30)	500	900	<20	<400		11.07	3.69		49.14
	(1.30-1.78)	600	1300	<20	<400		15.09	3.03		35.98
	(1.78-2.11)	600	1300	<20	<400		21.57	2.75		31.2
	(2.11-5.30)	1000	300	<20	1200		36.16	0.76		4.4

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G22**	(0-1.30)	3400	3500	50	1000		16.76	2.78		
	(1.30-2.5)	2500	1400	<20	500		5.12	5.01		
	(2.5-3.1)	750	290	<20	500		7.64	2.36		
	(3.1-9)	1100	560	<20	500		5.68	3.72		
	(9-9.4)	550	300	<20	500		5.75	2.4		
	(9.4-11.2)	<250	280	<20	<500		5.5	3.51		
	(11.2-11.5)	<250	270	<20	500		6.53	2.85		
	(11.5-12.1)	350	350	<20	500		6.91	3.47		
	(12.1-12.3)	350	330	<20	500		13.37	2.63		
	(12.3-12.9)	400	460	<20	500		6.41	3.57		
	(12.9-13.2)	450	430	<20	500		13.74	2.63		
	(13.2-14.6)	<250	280	<20	500		15.9	1.95		
	(14.6-14.8)	250	260	30	<500		26.27	1.33		

Sample		CONTAMINANTS, ppm					OTHER METALS, %			
Description	Depth (m)	Pb	Zn	Cd	As	S	Ca	Fe	Al	Ins.
Soils **G23**	(0-0.32)	32000	15000	100	1200		11.6	4.4		45.9
	(0.32-0.40)	25000	17700	100	1600		10.4	5.2		44.3
	(0.40-1.0)									
	(1.0-2.0)	12000	6600	40	400		11.2	3.78		50.6
	(2.0-3.0)	12000	570	30	400		12	3.37		50.1
	(3.0-6.0)	400	400	<10	<400		5.2	3.52		68.5
	(6.0-6.6)	200	200	<10	<400		22.4	1.8		31.94
	(6.6-7.0)	200	200	<10	<400		19.6	1.73		33.8
	(7.0-8.0)	500	400	<10	<400		12.4	3.02		50.32

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Λευκή οπίσθια σελίδα

SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION

LIFE Project, Contract No.: 93/GR/A/4/GR/4567

VOLUME 3

ENVIRONMENTAL CHARACTERISATION OF LAVRION SITE – DEVELOPMENT OF REMEDIATION TECHNIQUES

PHOTOGRAPHIC DOCUMENTATION

ATHENS, DECEMBER 1999

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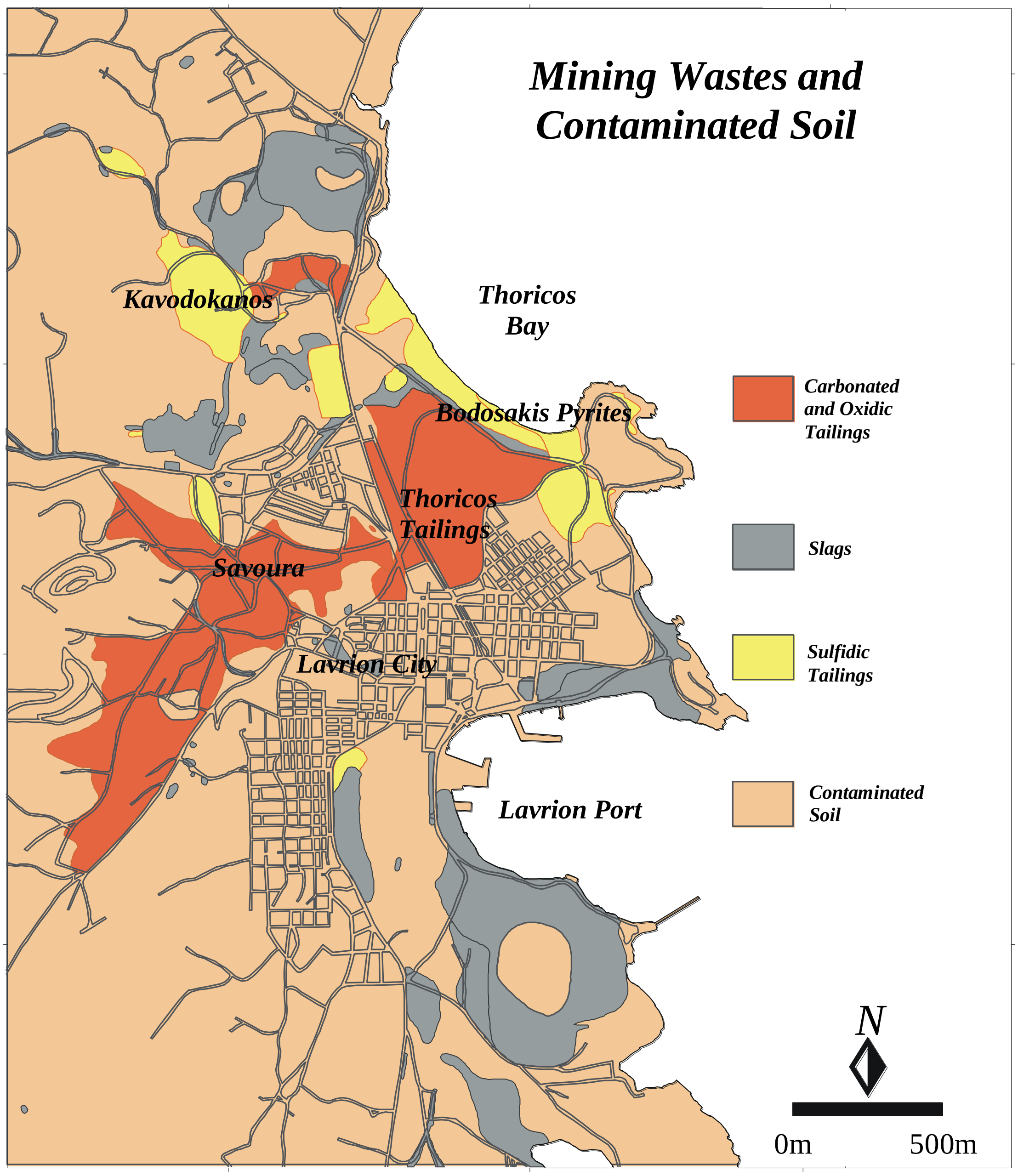
Λευκή οπίσθια σελίδα

Environmental Characterisation of Lavrion



Simplified map of metallurgical processing wastes and contaminated soil – Map 2.3, page 2.3 from Demetriades, A. (Editor), 1999. Geochemical atlas of the Lavrion urban area for environmental protection and planning. Volume 2: Maps. Soil Rehabilitation in the Municipality of Lavrion. EU LIFE Programme Contract No.: 93/GR/A14/GR/4576. Open File Report E-8272, Institute of Geology and Mineral Exploration, Athens, Hellas, 199 thematic maps in A3 size.

Απλοποιημένος χάρτης μεταλλουργικών απορριμμάτων και ρυπασμένου εδάφους – Χάρτης 2.3, σελ. 2.3 από: Δημητριάδης, Α. (Συντάκτης), 1999. Γεωχημικός άτλας της αστικής περιοχής του Λαυρίου για περιβαλλοντική προστασία και σχεδιασμό. Τόμος 2: Χάρτες. «Αποκατάσταση Εδάφους στο Δήμο Λαυρίου», EU LIFE programme Contract No.: 93/GR/A14/GR/4576. Έκθεση E-8272, Ινστιτούτο Γεωλογικών και Μεταλλευτικών Ερευνών, Αθήνα, 199 θεματικοί χάρτες σε μέγεθος A3.

Photo 1. Acidic water accumulated on the surface of Bodossakis pyrites at Thoricos bay.

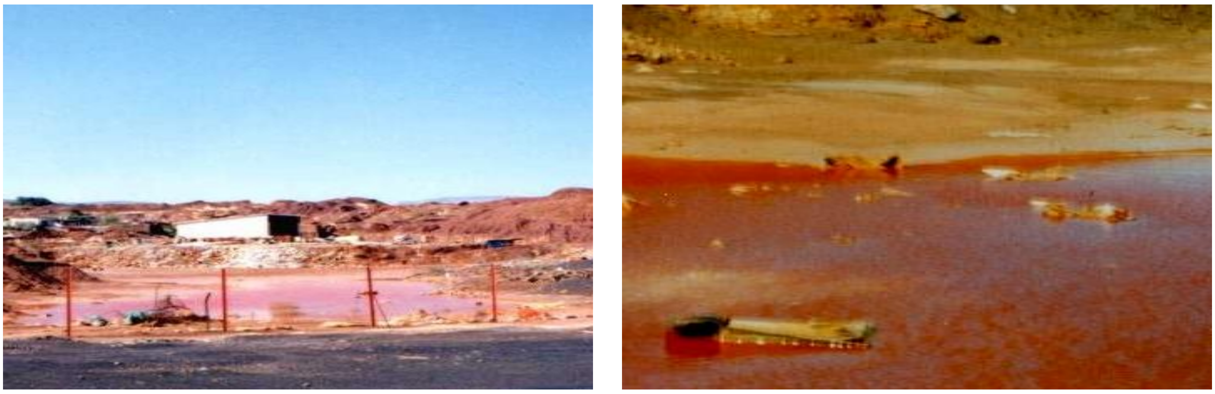


Photo 2. The heap south of Kavodokanos pyrites wastes and the generated acidic water.

Photo 3. The north heap of Kavodokanos pyrites.

Photo 4. Houses at the top of Kavodokanos pyrites wastes.

Photo 5. Agricultural activities on the top of Savoura tailings.

Photo 6. Oxidic tailings at Thoricos Bay.

Photo 7. Local inhabitant gathering herbs on contaminated soil.

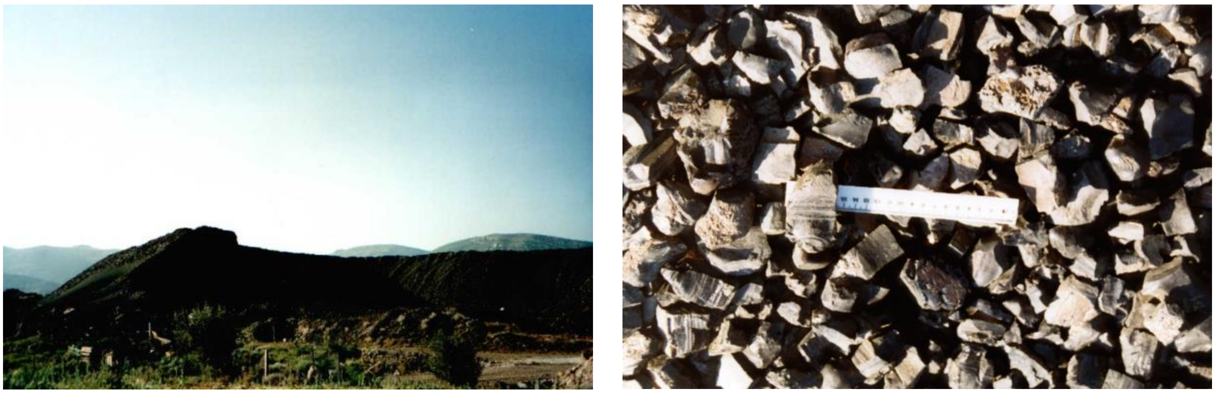
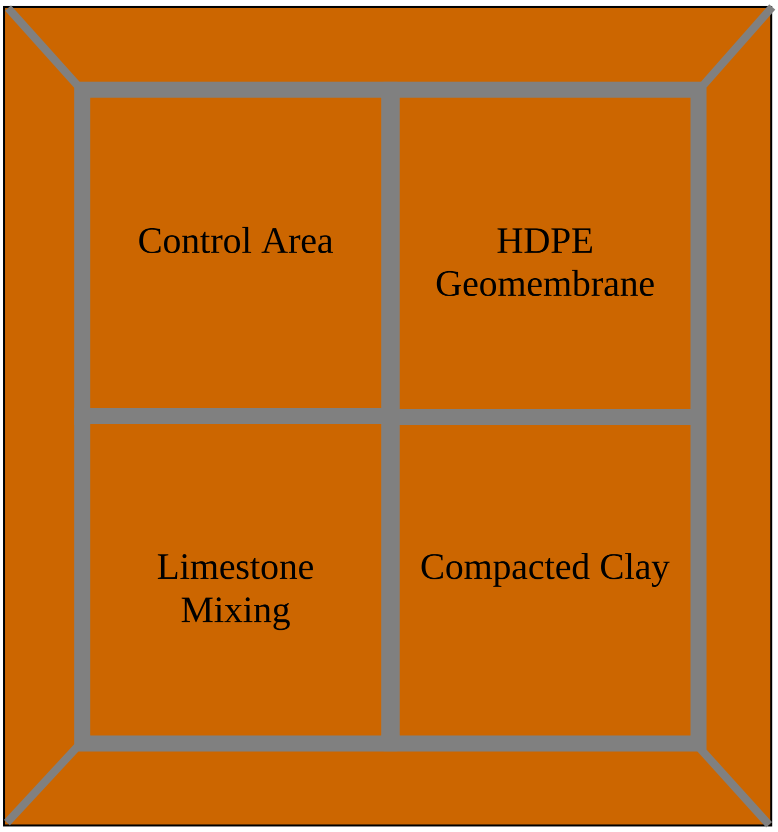


Photo 8. Slag heap on the left and close-up of slag fragments.

Rehabilitation of Sulphidic Tailings
Demo-Scale Application at Kavodokanos Pyrites



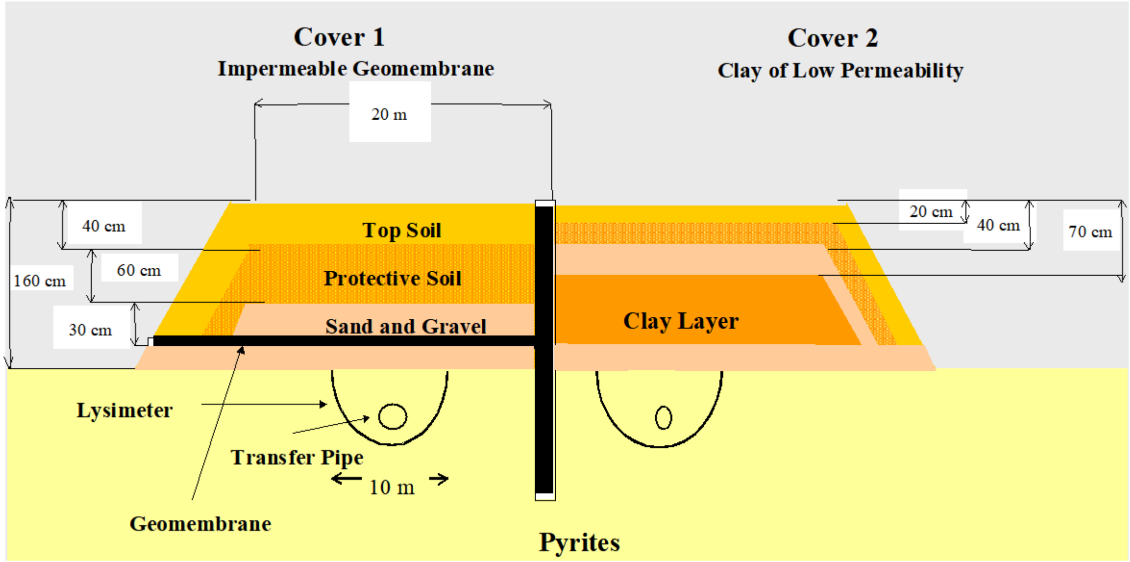


Photo 9. Installation of vertical geomembrane liners for the isolation of test plot areas.

Photo 10. Installation of the lysimeters (left) and the geomembrane (right).

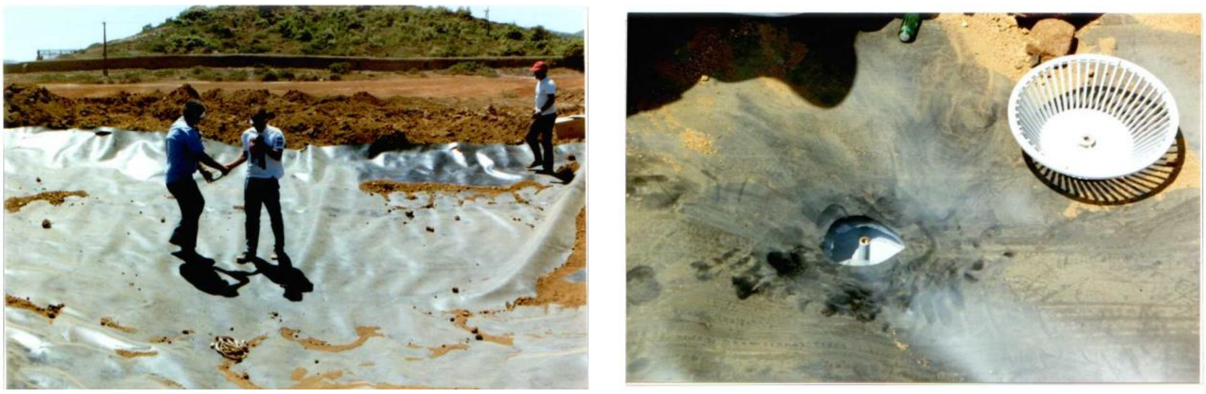


Photo 11. The installation of water collection system at the bottom of lysimeters.

Photo 12. HDPE Cover. First layer, 30 cm of fine gravel as capillary barrier.

Photo 13. HDPE Cover. Geotextile for the protection of geomembrane.

Photo 14. HDPE Cover. The geomembrane liner.

Photo 15. HDPE Cover. Welding of geomembrane sheets.

Photo 16 . Compacted Clay Cover. Watering of the clay layer.

Photo 17. Compacted Clay Cover. Compaction of the clay layer.

Photo 18. The excavation of Bodossakis pyrites from Thoricos bay.

Photos 19. The deposition of Bodosakis pyrites at the Kavodokanos test area.

Photo 20. Mixing of pyrites and limestone using a tractor.

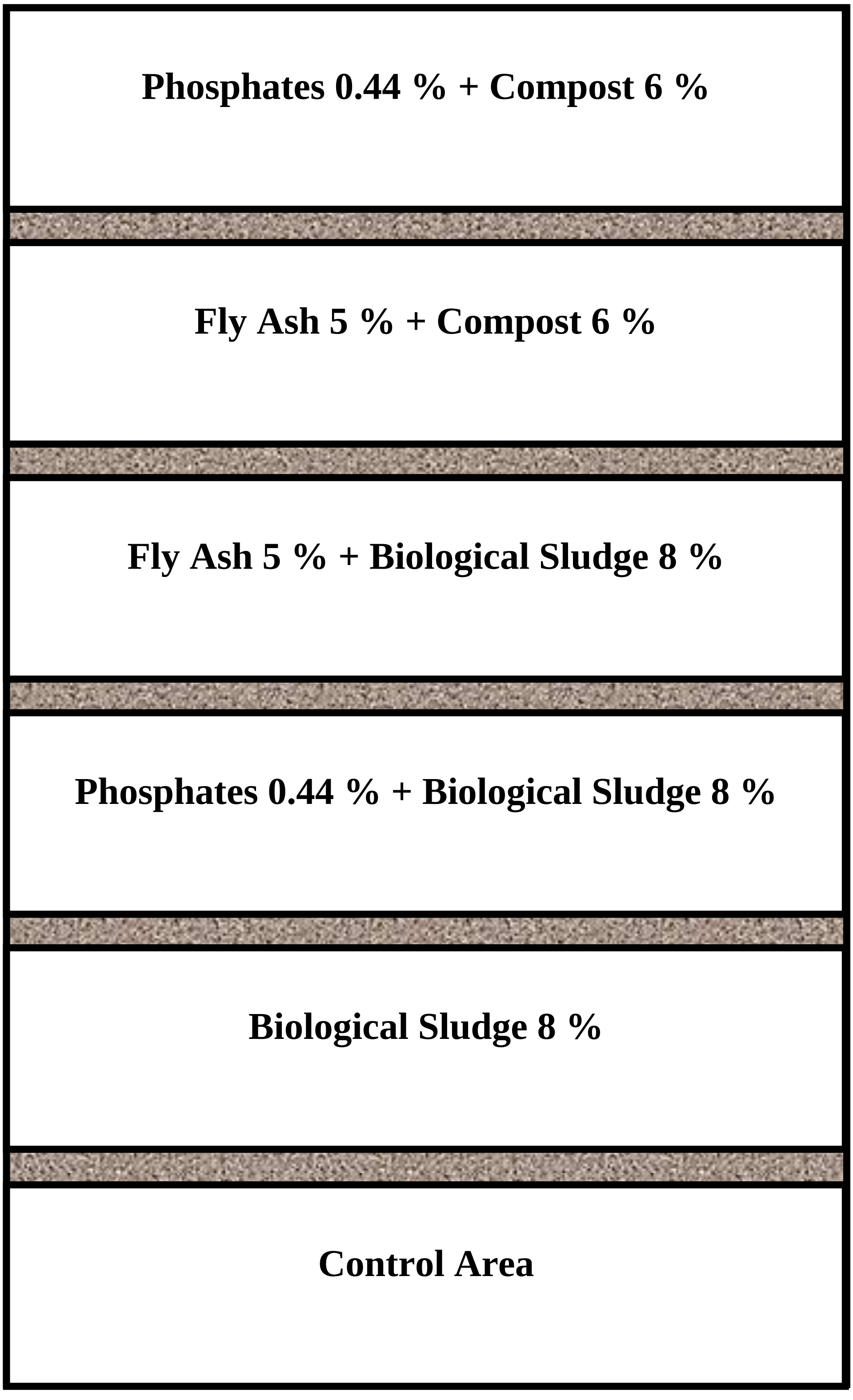
Photo 21. Control plot.

Photo 22. The four plots.

Photo 23. Tanks for the collection of percolated water through the four test plots.

Photos 24. The landscape of Kavodokanos before and after the works undertaken for the installation of LIFE demo-scale applications.

Chemical Stabilisation of Contaminants: Field Tests on Savoura Tailings



Photos 25. Pot experiments for evaluating the impact of several stabilising additives on the growth of plants and the phytoaccumulation of contaminants.

Photo 26. Stabilising materials used in the field tests.

Photo 27. Phosphate fertiliser.

Photos 28. Fly ash from the Public Electric Power Station of Ptolemais.

Photo 29. Biological sludge from the wastewater treatment plant of Metamorphosis.

Photo 30. Compost from the municipal solid waste pilot plant of Liosia.

Photo 31. Laying down of fly ash.

Photo 32. Laying down of compost.

Photo 33. Mixing of the flotation tailings with stabilisers.

Photo 34. Watering of the area.

Photo 35. The mixture of seeds used for sowing.

Photo 36. The Sower (Dec. 1997).

Photo 37. Mixing of soil and seeds (Dec.1997)

Photo 38. Overview of the area (Jan. 1998).

Photo 39. Overview of the area (Apr. 1998).

Test plot with Phosphates + Compost

Test plot with Fly ash + Compost

Test plot with Fly ash + Biological sludge

Test plot with Phosphates + Biological sludge

Test plot with Biological sludge

Control plot

Photos 40. Vegetation growth in the 6 stabilisation test plot areas (May1998).

Photos 41. Vegetation growth in the stabilisation plot areas during the 2nd growing period (December 1998).

Photo 42. Vegetation on the slopes of Kavodokanos pyrites (May1998).