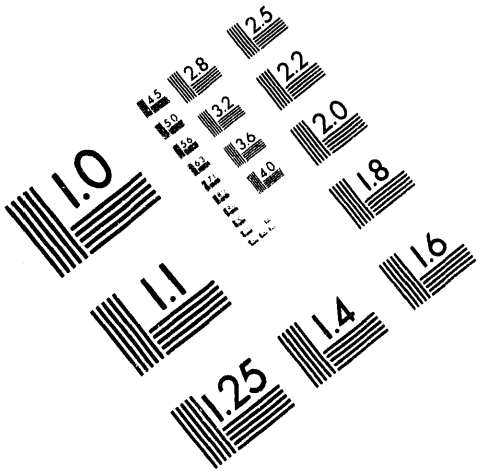

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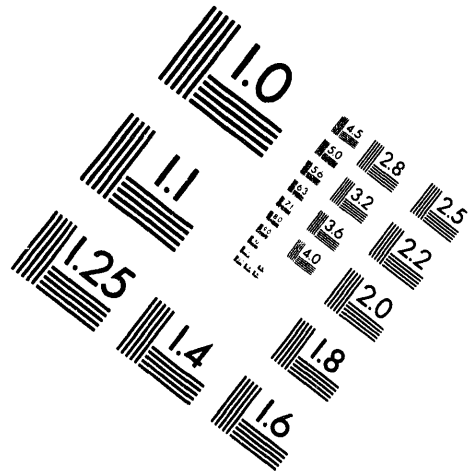

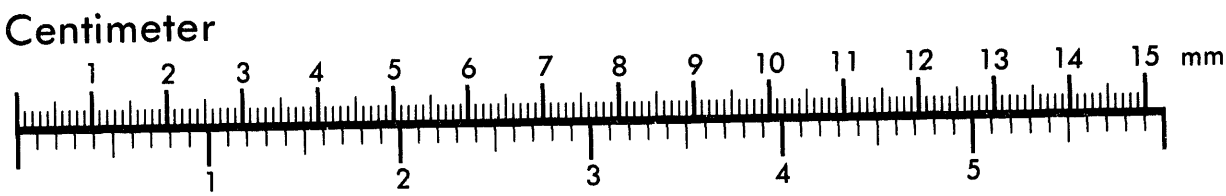


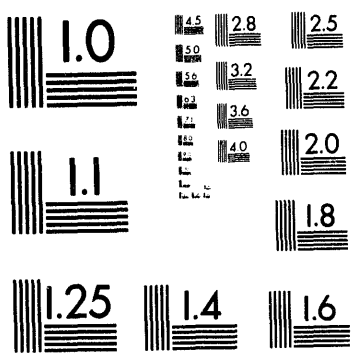

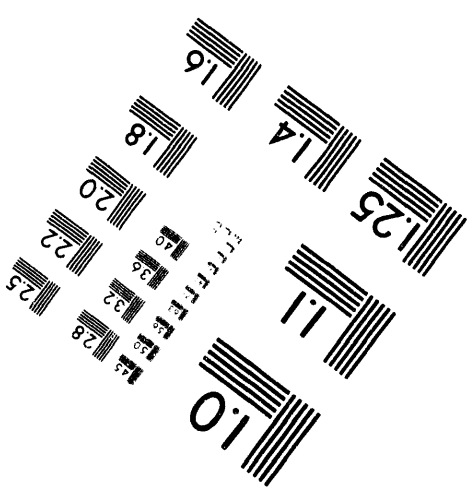

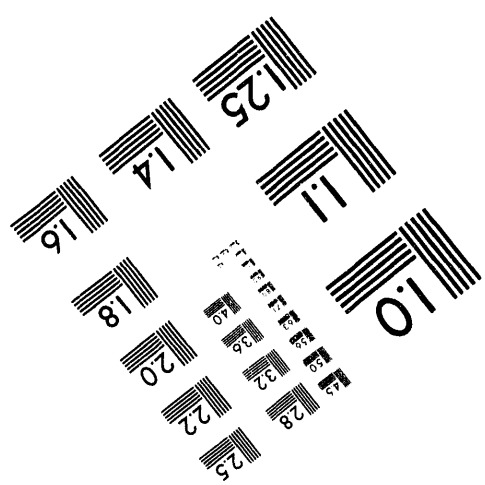

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# EVALUATION OF SOIL WASHING FOR RADIOLOGICALLY CONTAMINATED SOILS

Dirk Gombert II

March 1994

Westinghouse Idaho Nuclear Company, Inc.

PREPARED FOR THE
DEPARTMENT OF ENERGY
IDAHO OPERATIONS OFFICE
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# ABSTRACT

Soil washing has been applied internationally to decontaminate soils due to the widespread increase in environmental awareness manifested in the United States by promulgation of the Comprehensive Environmental Response, Compensation and Liability Act, yet we continue to lack understanding on why the technique works in one application and not in another. A logical, methodical approach must be designed to establish minimum acceptable criteria, determine what the controlling phenomena are, and then objectively evaluate whether the technology can potentially be applied to a site. Instead of solving the problem anew for each site, fundamental criteria based on soil science and engineering judgement must be established to build a knowledge base transferrable to the next situation.

A soil washing process typically integrates a variety of modules, each designed to decontaminate the matrix by destroying a particular phase or segregating a particle size fraction in which the contaminants are concentrated. The more known about how the contaminants are fixed, the more likely the process will succeed. Much can be learned from bioavailability studies on heavy metals in soils. Sequential extraction experiments designed to destroy one fixation mechanism at a time can be used to determine how contaminants are bound. This knowledge provides a technical basis for designing a processing strategy to efficiently decontaminate soil while creating a minimum of secondary wastes.

In this study, a soil from the Idaho National Engineering Laboratory was physically and chemically characterized, then sequentially extracted to determine if soil washing could be effectively used to remove cesium, cobalt and chromium. The contaminant distribution did not correlate with surface area or any particular crystalline phase. However, the transition metals did appear to be coincident with the matrix transition metals, iron and manganese. This finding was verified by sequential extraction data which showed that most of the cobalt and chromium were extracted by destroying the soil hydrated metal oxide phases. Unfortunately, less than 20% of the cesium was extractable even after dissolving over 20% of the

soil mass. The low recovery of cesium, the primary risk-driver, eliminated extractive soil washing from further consideration for this site.

# ACKNOWLEDGMENTS

The data was generated through a team effort and an exceptional commitment by personnel of the Analytical Chemistry Section at the Idaho Chemical Processing Plant at the Idaho National Engineering Laboratory. Special thanks go to J. H. Goettsche and G. M. Huestis for their support.

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# CHAPTER 1. DECONTAMINATION AND SOIL CHEMISTRY

## I. INTRODUCTION

"In the later 1480s the new technology became more diffused. For nearly a century thereafter Italian engineers scattered over Europe, from Madrid to Moscow and back to Britain, monopolizing the best jobs, creating wonderful new machines, building palaces and fortifications, and helping to bankrupt every government which hired them. To tax-paying natives they were a plague of locusts, but rulers in the sixteenth century considered them indispensable."

> - Lynn White, Jr. "The Flavor of Early Renaissance Technology," in Developments in the Early Renaissance, ed. B. A. Levy (Albany, 1972); p. 41.

The above quote, cited in Eugene S. Ferguson's insightful book Engineering and the Mind's Eye, MIT Press, Cambridge, MA, (1992), page 60, could be equally applied to our current engineering approach to technology development since the promulgation of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The law created extreme monetary incentives for timely cleanup, intended to bias industry to prompt action, and curtailed research. While good in theory, in that there is emphasis on restoring the environment, some actions have been misguided, creating greater risks due to waste disposition than those originally posed by the contamination, and we continue to lack understanding on why a technique works in one application and not in another. The literature is rife with erroneous claims based on extrapolating success from one location to the problems at another. Instead of solving the problem anew for each site, basic objective evaluation is necessary to build a knowledge base transferrable to the next situation.

Ferguson also discusses the loss inherent in giving up the slower slide-rule for the more precise calculator. Modern engineering is susceptible to loss of perception of the problem and solution. The "reasonableness" of the solution may not receive full consideration in our zeal for engineering analysis alone. He supports his argument with the results of a report generated by MIT in 1961 which states that engineering graduates may be too

likely to pursue only the problems that are amenable to analytical solution without consideration of the system. He attributes this to a curriculum focused on analytical solutions and modelling because they are unambiguous and therefore objectively measured to assign grades.

Judgement remains the primary requirement to sound engineering design. Technologies to clean the environment differ from those more well-documented in handbooks in two significant ways: first the payback is extremely subjective, so there is no quantifiable profit margin to work against, and second, the natural materials we must deal with are typically much more heterogeneous than pure industrial substances which makes them much less predictable and almost impossible to effectively model. This perspective is essential to this report which focuses on engineering judgement and systems analysis to develop a solution less burdensome than the problem.

Soil washing is one such technology developed to support environmental restoration, bringing to bear chemical and engineering sciences on the decontamination of contaminated sites. This technology may combine both physical and chemical processes to produce significant volume reduction of contaminated soils. While success has been demonstrated for organic and to some extent for metal contamination, review of available publications on practical applications to radioactive sites indicates that most volume reduction is a product of unique circumstances such as screening or floating out non-soil materials containing most of the contaminants, or leaching contaminants (uranium or TRU) that exist as anionic complexes[1] which are not held by the soil cation-exchange-capacity. In either case, the potential for success of the technology is extremely site and contaminant specific.

Environmental remediation techniques are based on the same principles used in mining, chemical manufacture, and water treatment. Nothing magic is implied by the environmental application; this new industry is just based on creative combinations of existing technology, with a little development

to reach new goals. However, due to the extraordinary costs of waste disposal, waste minimization has never been more critical.

A logical, methodical approach must be designed to establish minimum acceptable criteria, determine what the controlling phenomena are, and then objectively evaluate whether a technology can potentially be applied to the problem. The Environmental Protection Agency's (EPA) guidance on soil washing treatability studies suggests a 50% reduction of contamination in particles over 2mm as a reasonable cutoff for choosing soil washing for further development.[2] Once the decision has been made to attempt development, a systems approach is imperative to ensure a practical solution. The EPA guidance also suggests a concept not so well recognized; "Residual risk, as applied to soil washing, assesses the risks associated with treatment residuals ... sidestream and other treatment train processes should be included".[2] Soil leachants cannot increase the toxicity of the soil product, interfere with downstream water treatment, or present an unacceptable hazard to remediation workers. This "big-picture" approach is frequently lost in the drive to develop the "magic bullet".

This chapter includes a summary of the literature covering: 1) the state of the technology to date and the unique challenges of treating radioactively contaminated soils, 2) an introduction to soil chemistry and the mechanisms which can fix contaminants into the matrix, and 3) a strategy to evaluate if and how the technology should be employed.

## II. TECHNOLOGY DEVELOPMENT

### A. Mining Industry

A wealth of experience and knowledge is available in the mining industry on the recovery of precious and industrial metals. Commodity values have pushed retrieval efficiencies above 80% for ores containing parts-per-million (ppm) quantities of gold.[3] Crushing, screening, and grinding equipment for particle size reduction to enhance chemical contact, release

individual mineral grains, remove surface contaminants, and prepare material for particular applications or treatment comes in a wide variety of shapes and sizes. The chemical engineering Handbook by Perry devotes an entire chapter to these technologies.[4]

Physical separation requires a distinct size or density difference between the material to be processed and the reject material. Where the species of interest exists in distinct particles, screening, settling, or flotation may be applied to provide a first cut, such that more cost-effective processing can be targeted at the more concentrated media. The last two processes may be facilitated by chemical additions that are species specific and cause or accentuate density differences to promote settling or floating.

Acid leaching is typical of a chemical extraction to further concentrate the material for retrieval prior to purification for its intended purpose. Acid is relatively inexpensive, and metals can be readily removed from other soluble salts, so the gross dissolution of other acid soluble compounds is acceptable. Once the metals are removed, the remaining salt bearing solution can be dried to a cake in an open evaporation pond.

B. Soil Washing

Application of these technologies to environmental restoration purposes entails a set of more confining constraints, while trying to satisfy more demanding goals. Not only do the contaminants include organics and inorganics, with cleanup criteria which may be orders-of-magnitude lower than commercially valuable ore concentrations, but all effluents are subject to scrutiny for residual contamination. Surveys of soil washing as currently applied, particularly in Europe, show a key similarity in relying on size classification for the primary contaminant separation. Wet screening is used to remove particulate below a 63 to 74 micron cutoff range, which is then disposed of as hazardous waste.[5,6,7] Though chemical extraction may be employed in conjunction with the screening, it is

commonly accepted that fine particulate present in solution may resorb extracted contaminants, and it is not cost effective to continue to wash the fines. Soils containing more than 10-20% fines below the cutoff level are generally not cost effectively treated with soil washing.[5,6,7] Thus soil washing can typically reduce the volume of soil to be controlled by a factor of 5-10 by producing a small quantity of highly contaminated material while leaving the bulk soil mass relatively clean. However, the treatment does not actually reduce the toxicity of the contaminants.

While organic contamination is typically bound by the naturally occurring organic content of the soil[8], inorganic contaminants may be bound through any combination of several mechanisms including ion exchange, chemical and physical adsorption, precipitation, isomorphic substitution, and agglomeration. Adding to this complication is the extremely site and species specific nature of the problem. A soil washing flowsheet that works well to remove gasoline from a moist, humic soil would have a slim chance for success removing cadmium from an arid calcareous soil. Even a system proven successful for removing the same element from the same soil could have difficulty due to speciation, as is the case for trivalent versus hexavalent chromium. Applying soil washing technology to inorganic removal requires a quantum leap in sophistication from the relatively simple application of heated water and surfactants which can be quite effective for organic contaminants. Satisfactory results beyond size classification cannot be obtained for many metals in many environments.

C. Radioactive Contamination

Adapting this technology to radionuclide contaminated soils presents a much greater challenge. At the Idaho National Engineering Laboratory (INEL), for example, some contaminated soils and sludges are one-third to as much as three-quarters fine material below 50 micron.[9,10] In addition, the contaminants may not exist as individual particles. Being derived from aqueous solutions, many radionuclides contaminate soils on an atomic level. The contaminants are not limited to transition and heavy metals, but also

include alkalies and alkaline earth fission products that are chemically analogous to natural soil constituents which make up percent levels of the soil matrix. It is obviously questionable whether soil washing is applicable to these contaminants. More questionable is the ability to reach the radionuclide cleanup goals even if the conditions are ideal.

"How clean is clean?" takes on a special significance when radionuclides are discussed because instrumentation exists to measure radioactivity to extraordinarily low levels, and the risks projected by the cancer initiation models in use by the EPA have no lower bound.[11] To date, below regulatory concern (BRC) levels have not been quantified, and the waste disposition criteria for radionuclides in commercial landfills permitted under the Resource Conservation and Recovery Act (RCRA) have defaulted to background values, which vary by location, but are always very low. Continued placement of radioactive soils in Department of Energy (DOE) controlled landfills is complicated by the frequent association of radionuclides with regulated heavy metals and organics (mixed waste). The technology exists to treat most soils to the extent that they will pass the toxicity characteristic leaching procedure (TCLP) criteria under RCRA, but treatment may be complicated if not precluded entirely by the radioactive contamination. Chemically extracting metals to meet the TCLP requirements such that soils may be placed in landfills may leave a significant non-leachable metal content in the soil, but radionuclide limits are not simply a function of leachability. The very existence of radionuclides presents a cancer hazard as a function of proximity due to the non-contact effects of ionizing radiation. Obtaining contact handling standards of 5 millirem per hour for soils contaminated with cesium-137 requires contaminant reduction to parts-per-billion (ppb) levels. Treatment to eliminate all significant risks to allow free release, that is lower than the typically acceptable $10^{-6}$ levels (one additional lethal dose in a population of one million) for remediation efforts under CERCLA,[12] can require decontamination of radionuclides down to part-per-trillion (ppt) levels in the soil.[13]

Were it not for the potentially huge environmental gains to be made by

successfully developing soil washing for remediating radionuclide-bearing soils, the concept would have already been dropped. To develop an adequate knowledge base to definitively judge the usefulness of the technology requires some basic research in how the contaminants are bound, so flowsheets can be targeted at the controlling mechanisms. Without this knowledge, trial-and-error methods may never provide the results required to give the technology a comprehensive evaluation. It is very possible to free a species from one mechanism, while making it susceptible to another, with no net release from the soil. To obtain release, gross dissolution of an unnecessarily great fraction of the soil using acid may result in increasing the waste disposal problem. Without the basic knowledge on what binds the contaminant, it may only be fortuitous to develop an acceptable strategy.

## III. SOIL BASICS

### A. Fixation Mechanisms

Soil is a natural mixture of mineral and organic particles and their weathered derivatives. Contaminants may be found in a variety of forms including salts, ionically fixed ions, physi- and chemisorbed compounds, and several organic materials which may be ionic and/or covalent. The strong retention of radionuclides in some soils was once considered an asset because it served as a final barrier to contamination of ground water. This attribute is now a liability to returning contaminated soils to a near pristine condition for uncontrolled release. Understanding the fixation mechanism(s) is necessary to developing an effective strategy to induce release. The idealized soil particle in Figure 1.1 is labeled with six phases: 1) exchangeable ions, 2) precipitated salts, typically carbonates, 3) easily reducible metal oxides such as amorphous manganese oxides, 4) more refractory metal oxides such as crystalline oxides of iron, 5) organic matter, and 6) unweathered mineral lattice. This listing is not exhaustive, but representative of the phases which may be targeted for decontamination. More thorough descriptions of the chemistry involved may

be found in the references cited below.[14,15,16,17,18]

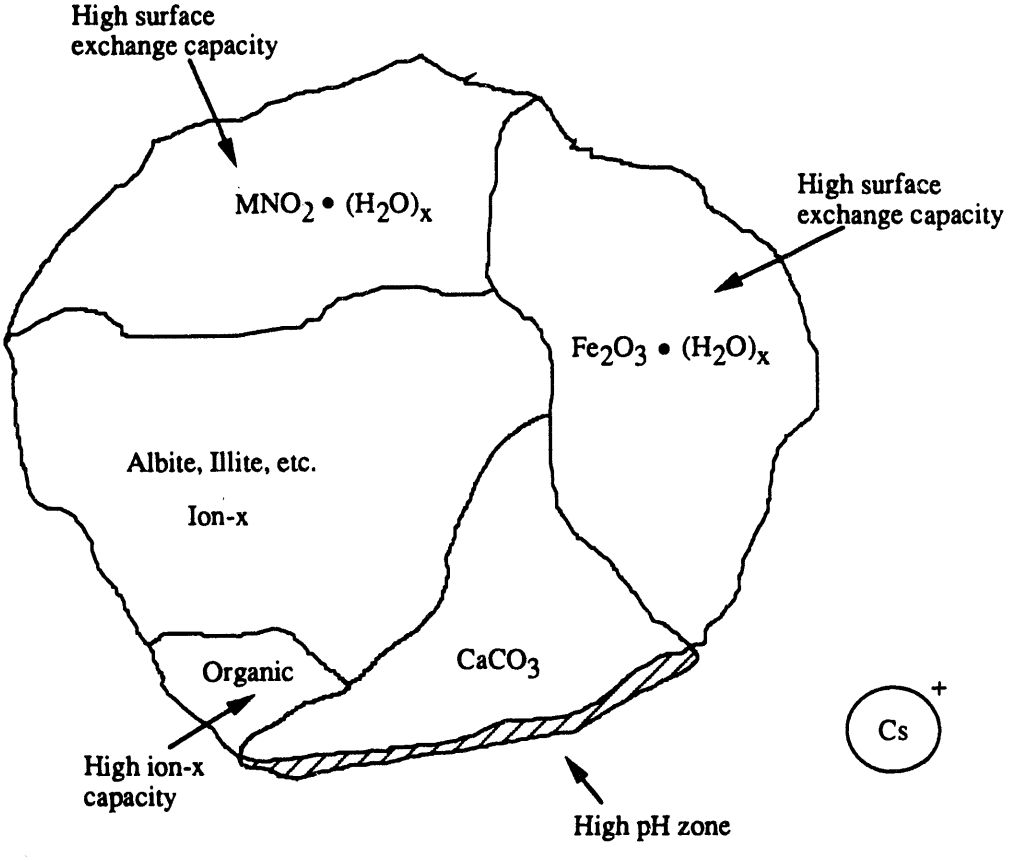


Figure 1.1 Idealized Soil Particle.

1. Exchangeable Ions

Many inorganic contaminants are held in soils by physical adsorption or cation exchange due to the electrical charge on soil particles, particularly clays. Cations are attracted to the broken edges of silicate layers to stabilize the negative charge imbalance that occurs where the silica tetrahedra are incomplete. The electroneutrality may also be upset by isomorphic substitution of an ion of lesser charge. For example, a trivalent aluminum or iron ion may substitute for a tetravalent silicon ion leaving the matrix with

a net negative charge.[14] This effect can be strongly influenced by pH; as pH is increased, the ability of water to stabilize the matrix is reduced, and the cation exchange capacity of the soil is increased.[14] Strontium has been shown to be less strongly bound by clays at lower pH values, probably due to reduced dissociation at hydroxyl sites (i.e., competition with hydrogen ions) and the net positive charge induced on aluminum and iron oxides.[15] Note that some contaminants exist in solution as anionic complexes or compounds and are held by analogous, but opposite forces. Some materials can be fixed in either manner depending on the soil redox chemistry and pH.

2. Precipitated Salts

Contaminants can also be deposited through precipitation from a saturated solution, coprecipitated with another material, or physically bound in an agglomerate due to the characteristics of another compound. As a solution evaporates, it eventually becomes saturated, and the salts crystallize on whatever solid surface to which they are exposed. Exposed to water again, these salts are typically redissolved. However, if they precipitate in pores where flow cannot be established, or as a new relatively insoluble compound, dissolution may be drastically limited. The local chemical equilibrium may also be controlled by pH such as in the carbon dioxide/carbonate/bicarbonate system which can cause fixation over a very sharp pH gradient around a carbonate mineral such as limestone.[16]

3. Hydrated Metal Oxides

Hydrated metal oxides are well known for their tendency to concentrate heavy metals. Oxides of aluminum, manganese, and iron readily hydrate to form a semi-continuous layer which may occlude other cations or particles.[14,17] Their effect may be disproportionate

to their concentration in the soil because they tend to form thin coatings on particles, yielding a tremendous surface area for fixing contaminants. Manganese oxides are primarily amorphous and readily reduced for dissolution. While iron oxides may be partially amorphous, the crystalline oxides require a stronger reducing agent. This difference allows the two types of oxides to be almost independently removed for study.

4. Organic Matter

Organic materials may also bind contaminants due to biological activity, stabilization by free organic ligands such as polyelectrolytes, or charge neutralization with organic acids.[16,18] Highly humic soils are typically acidic which tends to keep metals soluble, but also generally have a high cation exchange capacity (CEC) due to the activity of these other phenomena.[14]

5. Mineral Lattice

Over a long enough period of time contaminants may also substitute in a mineral lattice or diffuse into surface microfissures or pores to become trapped, in effect, becoming a part of the undissolved unweathered mineral fraction of the soil. Ironically, though this material is all but unavailable to the environment biologically, if radionuclides are involved, much investment may be necessary to solubilize them for removal.

B. Heterogeneity

As stated above, soil is a mixture of particles. Rather than the idealized surface depicted in Figure 1.1 with segregated patches of each phase, soil is a heterogeneous matrix of variable size, texture, chemistry, and contamination level. Though contamination generally concentrates in the finer material both due to surface area and the higher cation exchange

capacity of fine clay and organic particles, many factors can modify this general effect. Depending on its mode of deposition (alluvial, eolian, etc.), the climatic history, the parent mineralogy, and the contamination pathway, the matrix may range from coarse to fine, include all of the phases described above or be dominated by one or two, and may or may not be uniformly contaminated. Heterogeneity confounds the applicability of results from one location to another, and makes modelling almost impossible. Any testing must account for this variability by ensuring the sample is well mixed, and performing replicate analyses to check reproducibility.

## IV. TECHNOLOGY EVALUATION

### A. Preliminary Physical and Chemical Characterization

Certainly screening the material to determine if a significant fraction may be discarded without treatment is a sound start. Chemical assay of the soil fractions will not only identify which fraction(s) on which to focus, but analyses of other typical soil constituents may also provide initial insight into any correlations between the contaminants and compounds in which they could be fixed. These analyses will also provide the basis for understanding the soil chemistry, e.g. acidity, alkalinity, organic content, and fines fraction. For a small amount of soil, or a relatively straight forward decontamination, simple trial-and-error with the most widely used or most probably effective cleaning agents such as water (hot or cold), detergents, complexing agents, or possibly acid or caustic may be completely satisfactory to evaluate the efficacy of soil washing. For more complicated contaminants such as soil analogues, particularly with radionuclides where long term disposition and control drives waste minimization more than short-term costs, a more insightful strategy may be necessary. The more known about the contaminant retention in the soils, the more likely an efficient contaminant-specific release flowsheet will be developed. Not all trial and error can be eliminated from the R&D program, but certainly developing a hypothesis on the principal retention

mechanism(s) for a species in a particular matrix will provide a basis for organizing an experimental strategy.

The next step may include a surface analysis if possible. Though the contamination could penetrate into the individual particles over time, the contamination was introduced from an external source, and therefore should reside primarily on the surface. Elemental mapping of the surface with a scanning electron microscope (SEM) may corroborate correlations indicated by the chemical assays, or it may indicate less obvious correlations such as the disproportionate metal fixing capability of the hydrated metal oxide films described earlier. Electron spectroscopy for chemical analyses (ESCA), though expensive, may give direct indication of the compounds fixing the contaminants of concern.

B. Mechanism Identification

Though significant work has been done to quantify the relative retention characteristics of contaminants in soils, most of this research has been in support of migration modelling.[19] Very little work has been found in the literature on studies dedicated to defining how radioactive contaminants are retained. Other than generalities on cation exchange, very few mechanisms are even suggested. Contact with many commercial vendors of soil washing technology has explained the dearth of published data; virtually all testing data with RCRA regulated species is protected as proprietary, and little or no work has been done with radionuclides because of the regulatory morass which makes profitability questionable.

Much can be learned, however, from bioavailability studies on heavy metals in soils.[16,20,21,22] Sequential extraction experiments are designed to destroy one fixation mechanism at a time, progressing from relatively mild to increasingly more aggressive treatments. Chemical analyses of both the solids and the leachate between steps suggest the mode of fixation for each contaminant. The challenge is in designing a treatment that will efficiently eliminate one mechanism, without attacking the remaining

matrix. Not only is this ideality impossible to fully attain, it can be masked by the refixation of the contaminants in the remaining solids. In addition to providing step-wise release data for the contaminants of concern, the chemical analyses can help to adjust the extraction procedure by providing verification of how completely a phase is removed, and some insight into the unavoidable attack on the remaining mechanisms. Though imperfect, this technique can be used to deduce the most probable fixation mechanism so that it may be targeted by a flowsheet.

Summarized in Table 1.1 are some of the reagents listed in the references cited above to perform selective leach experiments. This is by no means a comprehensive list, and reference to the original publications and bibliographies contained therein is recommended for evaluating which treatment is most applicable to a given soil. The leachants are listed by mechanism attacked, in the order of the typical sequential design. The first leach should be dedicated to physical adsorption and ion exchange, the second carbonates, etc. The following paragraphs summarize some of the considerations important to selecting leachants.

Some of the ion exchange solutions may also attack calcium carbonate either due to the acetate complexing the calcium, or the ammonium ion neutralizing the carbonate.[16] Running the extraction at a pH slightly over 8 rather than in a neutral solution may mitigate the complexing effect, and using the sodium salt may eliminate the neutralization problem.[16] In addition to pH, the time and temperature of the extraction should be held constant, experiment to experiment, to minimize data variability.[16]

Reducible metal fractions may be altered during sample preparation, such as exposure to air for samples from reducing environments.[16] Metal oxide films are surface active due to their hydrated surface. Samples should be washed with only deionized water, and dried to constant weight at a temperature below the boiling point. Drying in an oven may drive off some or all of the waters of hydration, changing the natural characteristics of the soil.

| Table 1.1 Mechanism Specific Leachants | |
|---|---|
| Target Mechanism | Extractant |
| Exchangeable Ions | 0.05 M $CaCl_2$<br>$BaCl_2$, Triethanolamine, pH 8.1<br>$MgCl_2$, pH 7<br>$NH_4OAc$, pH 7, 8.2<br>NaOAc |
| Precipitated Salts | $CO_2$<br>NaOAc/HOAc buffer, pH 5 |
| Hydrated Metal Oxides | Acidic Hydroxylamine<br>Ammonium Oxalate Buffer<br>Hydroxylamine/Acetic acid<br>0.1 M $NH_2OH/HCl$, 0.01 M $HNO_3$, pH 2<br>0.2 M Ammonium Oxalate, 0.2 M oxalic acid, pH 3<br>Ammonium oxalate/Oxalic acid with UV<br>Sodium Dithionite-citrate buffer<br>Hydroxylamine/HCl, Acetic acid |
| Organic Matter | $H_2O_2$, $NH_4OAc$, pH 2.5<br>30 % $H_2O_2$, 0.02 M $HNO_3$, pH 2, 85°C<br>Organic Solvents<br>0.1 M NaOH, $H_2SO_4$<br>Potassium pyrophosphate |
| Mineral Lattice | $HNO_3$ (conc.), 180°C<br>Aqua Regia, HF, Boric acid<br>$HF/HClO_4$ |

Chelating, and complexing effects of leach solution anions may also yield confusing results for metals.[16] Reprecipitation may occur due to pH swings at particle interfaces, or in the solution due to loss/gain of carbon dioxide.[16] Adjusting the pH up to 3, and decreasing the contact time to 15 minutes and the reagent concentration to 0.025 M may make the hydroxylamine hydrochloride leachant even more specific, removing the more readily reduced manganese oxides while leaving the iron oxides virtually intact.[23]

Using sulfide bearing reagents may cause low solubility metal-sulfides to be lost from solution.[16] Care should also be taken in using dithionite because of inherent zinc contamination, and residual extractant can cause

plugging problems in atomic absorption equipment.[21]

Sodium and potassium chlorides have also been used to displace strontium and cesium.[24] Calcium chloride was shown to effectively displace strontium which might be expected from their chemical similarity, but potassium seemed to be far more effective at displacing cesium than was sodium which suggests some sort of steric hinderance rather than simple ion exchange.[25]

Chelants have also been used to extract heavy metals from soils,[26] but are notably absent from Table 1.1. These materials enhance solubility, but provide no mechanism specific attack, and therefore are not particularly effective for a sequential leach.

## V. CONCLUSIONS

The need for R&D to minimize the amount of waste our societies will have to control for years to come is without question. Though trial-and-error testing is quick and relatively inexpensive, it provides little or no insight for technology transfer to other locations. A mechanistic approach yields enough data to help explain how a process works or why it should not be considered further. With this level of understanding, it will be easier to present the evaluation as comprehensive to local communities. Finally, developing flowsheets to minimize waste by minimizing the amount of soil dissolved is cost effective.

Timely treatability studies are necessary to evaluate the potential for technologies such as soil washing for application to radionuclide contamination. The goal of the research should be to provide adequate insight into the physical/chemical processes involved to determine if soil washing should be considered for remedial actions with radioactive soils. Soil assays, surface analyses and sequential leaching strategies are tools available to provide the knowledge base needed to make informed decisions.

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# CHAPTER 2. SOIL WASHING TECHNOLOGY

## I. INTRODUCTION

Soils contaminated with heavy metals and/or radionuclides pose a significant health threat and a huge international financial burden for clean up and disposition of the resultant waste. The international industrialized community is faced with the responsibility of managing the health and environmental risks posed by millions of cubic yards of soils contaminated with radionuclides. These soils were contaminated by a broad spectrum of activities ranging from uranium processing tailings and solution mining wastes, to historically accepted soil column and landfill disposition of contaminated wastes, to accident scenarios (i.e., Chernobyl, Johnston Atoll) and war time events, including nuclear weapons production, testing and use.

Though significant funding and emphasis has been directed toward developing new technologies, physical and chemical soil washing are the only options available for decontamination of these soils. Physical soil washing is the use of materials handling equipment, mostly borrowed from the mining industry, to separate particles over a gradient of some physical characteristic, e.g., density or nominal diameter. Chemical soil washing involves the use of an extractant to dissolve some fraction of the matrix to release the contaminants on a molecular or atomic scale. Though much development has been directed toward more efficient means of decontamination, little basic research has been published to explain the correlation of successful treatment with the mechanism responsible for fixing the contamination in the soil matrix.

A responsible engineering design should begin with an understanding of how the contaminants are fixed so that a process can be designed to target the contaminated phase(s). Each of the mechanisms described in Chapter 1 can be targeted by a unit operation rather than attacking the soil as a whole. This approach should not only minimize secondary wastes requiring

treatment, but allow a definitive judgement of whether the technology is applicable at a particular site. This chapter covers a detailed description of the operations used in soil washing, including an explanation of how the mechanisms described earlier can be targeted in particular steps.

## II. WASTE MINIMIZATION

Decontamination of radioactively contaminated soils is complicated not only by the heterogeneous nature of soil, but also by the wide variety of radionuclides including transition metals, alkalies, alkaline earths, and uranium and transuranic elements. In addition to the technical complexities, however, the legal issues of cross-contamination with hazardous wastes (a complete description may be found in the code of federal regulations, 40 CFR Part 261) and disposal are extremely restrictive. The importance of waste minimization in process design cannot be over-emphasized. The following is a brief summary of the legal background of this constraint.

In the United States, since the landmark case filed by the Legal Environmental Assistance Foundation (LEAF) against Hodel (the Secretary of the Department of Energy (DOE) in 1984), the Environmental Protection Agency (EPA) has had shared jurisdiction over the management and disposition of defense-activity wastes which exhibit both hazardous and radioactive properties. Prior to that time, the DOE held that all radioactive wastes created by their activities were exclusively managed by DOE contractors under the special nuclear material and by-product exemption provided by the Atomic Energy Act (AEA) of 1954. The court's finding in LEAF v. Hodel, restricted the AEA exclusion to protection of information only to the extent that national security was affected. In 1987 the by-product rule was modified to yield EPA control over the nonradioactive fraction of the waste, and finally, in 1988 the EPA formally decreed the category of "mixed-waste". A similar arrangement is in place between the Nuclear Regulatory Commission (NRC) and the EPA for commercial (i.e.,

utility and medical) wastes.

Disposition of mixed-wastes, regulated by two agencies, creates challenging opportunities for an engineer designing a process to treat soils cost-effectively. Interestingly, wastes contaminated with sufficient hazardous wastes to be governed by the Resource Conservation and Recovery Act (RCRA) must be disposed of in landfills with very prescriptive design features such as double-liners, leachate collection and groundwater monitoring. Radioactive-only wastes are governed by their activity level and nuclide inventory, but can be disposed of in a landfill which is essentially a "hole in the ground", so long as they meet relatively simple waste acceptance criteria, (i.e., no pyrophorics, free liquids, finely divided solids, etc.) Obviously, to mitigate the costs of excavation, packaging, and long-term management, segregation of wastes is extremely important.

Physical segregation is certainly the preferable alternative, because it generates only minimal secondary wastes. Chemical extraction is a last resort attempted only if a unique chemical advantage is gained, or if no other option is available. Though much effort has been expended on solubilizing contaminants, treatment of secondary wastes has generally been assumed to be within the spectrum of traditional low level radioactive solid and liquid waste treatment.

Complicating this assumption is the mixed-waste issue. There is no de minimis level for radioactivity other than possibly local background levels. Additionally, there are specific treatment and concentration guidelines for hazardous constituents per RCRA regulations. The best strategy is to minimize the secondary waste streams and, to the extent possible, segregate the radionuclides from the RCRA hazardous constituents.

# III. PROCESS DESIGN

## A. Modular Design

A soil washing treatment process is typically built from skid-mounted modules which might include some or all of the basic steps combined in Figure 2.1. This allows the process to be tailored to a specific site, and reconfigured after mobilization to a new site. Physical segregation is used to the extent possible, to minimize the amount of material requiring further treatment. If satisfactory results are obtainable, the only liquid used is locally available water. Chemical extraction, if necessary, is targeted primarily at the fine fraction, but some use of extractant may be advantageous during the physical separations to take advantage of the agitation and intimate mixing. Recycle of the wash solution is critical to the success of any process due to the huge volumes of material to be treated. This not only minimizes the volume of water required, but more importantly reduces the effluent to be treated. A certain minimum blowdown stream is unavoidable even in a purely physical wet process, however, due to the solubility of naturally occurring salts and the buildup of suspended solids and/or colloidal material that cannot be readily filtered.

## B. Oversize Material Separation

An adjustable bar screen is commonly used to separate oversize rock, roots, and debris which might interfere with the downstream processing equipment. This large material normally meets decontamination criteria based on weight because of its low surface area to volume ratio. The bar spacing is set at the smallest practical size that will yield a reject pile that can be disposed of without further treatment, typically 2-6 inches. If even the large material contains too much contamination to be returned to the excavation, it may require size reduction such as shredding or crushing for further processing. In unique circumstances, such as piles containing discrete pieces or agglomerates of contaminated media, separation may be achieved by manual sorting.[1] If the pile is small enough, however, it may

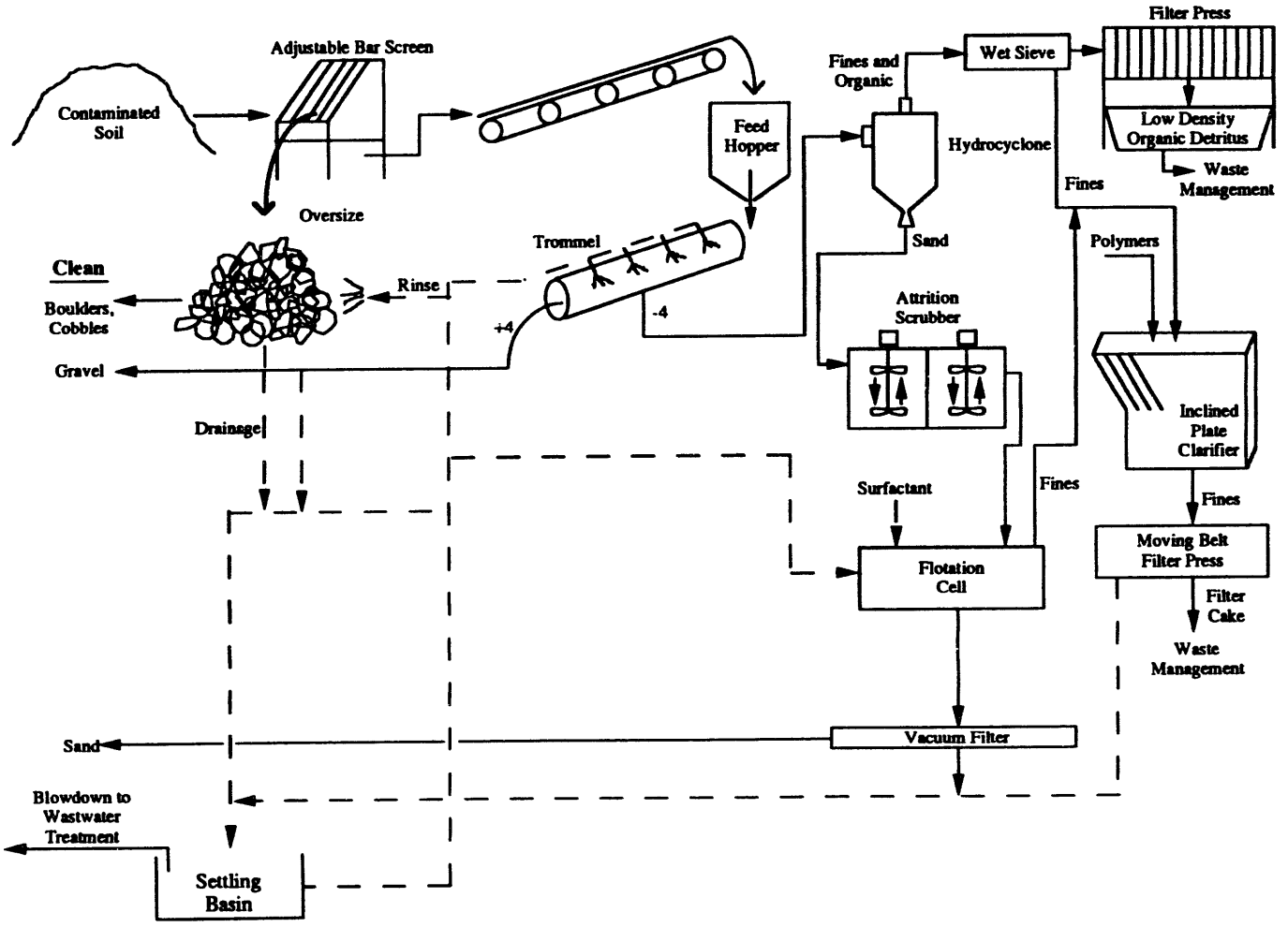


Figure 2.1 Conceptual Soil Washing Process

be more cost effective to package the whole pile for waste management.[2]

C. Trommel

A trommel is an inclined rotating cylindrical screen or set of screens which provides a rough separation as material is tumbled. Though typically incorporating a water spray to mitigate release of contaminated dust, this processing may be done dry if dust is not a significant factor. The tumbling action serves to break up lightly bonded agglomerates and to separate gravels from sand and finer material. In many cases the gravel fraction can also be returned to the excavation without further processing.

The trommel is also the first opportunity to aid decontamination by adding an extractant. Water will probably suffice if the gravel is only contaminated by fine particulate bonded to surfaces statically, or agglomerated by materials such as clays or organic material. Time in the trommel is limited, so realistically the material can only be rinsed in this step, but if a precipitated salt is readily soluble in a solvent, or a solvent is to be used in the liquid circuit for downstream processing, using the same solution in the trommel may provide additional decontamination.

D. Sizing

The next particle size separation may be accomplished by a series of hydrocyclones (as shown), vibrating screens, or screw classifiers. All units provide a rough separation of sand from finer material primarily by particle size, but much of the low-density organic particulate will separate with the fines cut from the hydrocyclone. If most of the contamination is bound by ion-exchange, it should be found primarily in the fine material which contains the clays and organic matter. In some cases, the sand fraction will meet the decontamination criteria without further processing, but if significant contamination is bound on the grain surfaces, some form of surface abrasion may be necessary.

If treatability studies (laboratory tests) indicate significant contamination is contained in weakly bound organic matter or surface coatings, separation through a mineral jig may be used to pretreat the feed to the hydrocyclones or replace them altogether. A mineral jig is a pulsed up-flow classifier incorporating a layer of steel shot or gravel on a screen through which the settling particles must pass. If the contamination is only weakly adherent to the sand grains, this additional agitation may be adequate to break the contaminated particles free to be carried out in the rising solution.[3]

E. Attrition Scrubbing

For more adherent coatings, simple autogenous grinding may be necessary. In an attrition scrubber, a particle slurry is passed through a highly turbulent zone between opposed impellers, causing attrition of the particle surfaces by impingement of other particles. This abrasion can be controlled to remove surface films such as precipitated salts and/or hydrated metal-oxides. The remaining solid core should then meet the decontamination criteria.

F. Flotation

An air flotation cell is used to separate low density organic matter and fines from heavier mineral particulate by attaching gas bubbles to the contaminated fines causing them to float to the surface to be skimmed. As shown in Figure 2.1, a flotation cell is used to separate the fines generated (and dislocated) in the attrition scrubber. Surfactant is mixed with the slurry to make the particulate hydrophobic causing it to float to the surface as the slurry is sparged. Choice of reagent addition is based on laboratory testing to produce the most efficient separation of contaminated media.

## G. Dewatering

Dewatering of the fines is required because waste shipped to a landfill cannot contain any free liquids (dewatering may also lower disposal costs which are on a weight basis). Polymer is added to produce a floc to enhance settling in a clarifier. The settled sludge is then pressed to remove free liquids prior to shipment.

Fine solids from the rough separation step may be further divided prior to dewatering if laboratory testing indicates contamination may be segregated in organic or fine mineral material. This may be possible using a vibrating screen (as shown in Figure 2.1) or a flotation cell.

The sand fraction may be dewatered efficiently using a vacuum filter as shown, or more slowly by allowing time for gravity draining. All solutions from dewatering are recovered for recycle to the process. A settling basin and some degree of additional water treatment are typically required if any contaminants are soluble.

# IV. CORRELATION WITH SEQUENTIAL EXTRACTION

As noted in the process descriptions above, each of the mechanisms which can be selectively extracted can be targeted in the soil washing process. Ion-exchangeable material is primarily bound in the fine mineral and organic fractions which account for most of a soil's cation exchange capacity. Some precipitated salts are readily soluble with a slight pH adjustment, or a particular solvent. Less soluble salts and metal-oxide coatings may be abraded to yield a clean mineral core. Finally, if significant contamination remains with the mineral grains after all steps, extractive soil washing cannot be used. Decontamination would require gross modification of the soil matrix such as dissolution in mineral acids or milling to liberate contaminated fines trapped in microfissures. With radioactive contamination, this type of processing would almost certainly result in an increased waste volume.

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# CHAPTER 3. RELEASE AND RESORPTION

## I. INTRODUCTION

Much can be learned from sequential extraction methodology described in the first chapter wherein the soil matrix is chemically dissected to selectively dissolve particular soil components independently. However, the published studies do not appear to consider the potential for a contaminant released from one type of site to resorb on another site during an extraction. Chemically or physically removing a phase may generally act to the benefit of removing a contaminant, but a layer may cover or block pore spaces or ion exchange sites, and removal may open these other sites for active fixation. If resorption is significant, it is doubtful whether a sequential extraction, no matter how ideally selective, can provide representative data on the actual distribution of contaminants by phase or fixation mechanism.[1] Treatability studies may erroneously conclude that a contaminant cannot be removed, when in fact control of resorption is all that is required. Therefore, characterization of the relative magnitude of resorption during soil decontamination is essential to definitive evaluation and may provide the insight necessary to improve the technology for wider application.

## II. BACKGROUND

### A. Sequential Extractions

The sequential extraction methodology referenced above uses a series of progressively more aggressive solvents to dissolve six principle phases: 1) exchangeable cations, 2) precipitated carbonates, 3) easily reducible metal oxides (primarily amorphous oxides of manganese), 4) more refractory metal oxides (primarily crystalline oxides of iron), 5) organic material, and 6) the residual mineral lattice. In step one a brine is used to displace exchangeable ions and in step 5 a brine is added to mitigate resorption after the organic matter is destroyed. In step six the residual

mineral solids are completely dissolved. However, in steps 2, 3, and 4, the published studies do not consider the potential for a contaminant released from one type of site to resorb on another site during an extraction. The physical model assumes, in effect, no ion exchange or adsorption at sites either previously occupied by other ions, or exposed by the dissolution.

It is typical in the literature, that a significant percentage of heavy metal contamination (up to 50 wt.%) is concluded to be fixed in the residual crystal lattice. While this is certainly possible; clays have extensive capacity for ion exchange, and silicates may have considerable capacity at unsatisfied lattice edges, substituted sites or at intercrystalline boundaries, it is also possible to free a species from one mechanism, while making it susceptible to another, with no net release from the soil. These results may be influenced by a cascade of ions from one type of site to another as the most active fixation sites are destroyed by dissolution.

The tendency for an ion to exchange at an uncovered site will be a function of the Hofmeister Series which takes into account the ionic charge and hydrated radius.[2] Generally, the greater the charge and smaller the hydrated radius, the greater the charge density, and the stronger the affinity for a charged substrate. Therefore a contaminant ion may displace an ion of lower affinity to resorb on the surface thereby decreasing the apparent degree of decontamination.

B. Research Needs

Ideally, if one were characterizing a spill of limited extent, such that uncontaminated material of a similar nature was available just outside the spill area, comparative studies on adsorption could be characterized in parallel with extraction from the contaminated material. However, even in this unique circumstance, there would still exist the basic unresolvable questions including the influences of weathering, time and temperature on

the contaminants and their distribution. This simplistic goal is made more challenging by the heterogeneity of natural materials such as soil and the complexities of the soil matrix. Grinding the soil, using only a narrow particle size fraction, or any other technique which might normally be used with synthetic resins or catalysts to isolate specific physical phenomena, may modify the characteristics of the native soil matrix reducing the credibility of the experiment.

Clearly, many of these shortcomings can be avoided if the release and desorption phenomena can be evaluated separately for the same soil. One approach is to cause release of the contaminant without allowing it to resorb. This can be accomplished by borrowing from a technique used for developing elution profiles in ion-exchange chromatography. This analytical method accomplishes the isolation of two or more ions by taking advantage of the difference in their relative affinities for a solid substrate. Following a loading phase, the species are eluted by passing a clean solution through the exchange column. As the species are washed through the column, they continue to desorb and resorb, proceeding down the column while in the liquid phase in a random walk fashion.[3] Though the bulk of a particular species washes out as a front, this random walk creates some distribution around the front which creates a following tail of diminishing concentration. Because the adsorption isotherm is typically not absolutely linear, and the relative extent of adsorption is greater at lower concentration, the tail continues to grow, which may blur a following peak. To enhance the separation, the eluting solution may contain a counter-ion specifically selected to prevent the resorption of the species of interest by actively competing with it for available sites.[3,4] This "displacement development" can be accomplished using an ion of greater adsorption affinity for the substrate or by concentration (as in ion exchange regeneration) or both. Thus, by conducting parallel extractions, with and without the counter-ion present, the effect of resorption can be isolated, allowing its relative magnitude to be evaluated.

# III. KINETIC MODEL

## A. Dissolution

The metal-oxides in a soil may represent a significant portion of the contaminant fixing capacity of the matrix. This is attributed to the very thin (possibly only several atomic layers) but high surface area film a hydrated metal oxide may form on an otherwise virtually inert particle such as a quartz grain.[5,6,7] If a first-order reaction is assumed, the rate of selective dissolution of the iron oxide film at constant temperature reduces to a function of surface area and solvent strength:

$$dC(Fe)/dt = kAC(solvent),$$

where: C represents the concentration in the liquid phase, A is the surface area of dissolving iron oxide film, and k is a rate constant (mg/l/s).

No other time-dependent source term is included because the experiments are to be done in nonmetallic containers. Also, no loss term is necessary because all iron dissolved out of the oxide should be kept in solution by the iron specific extractant/complexant.

If the film is uniform, and indeed very thin, the differential radius of the particle across the film approaches zero, and the surface area may be assumed constant until the film is gone. Similarly, if the film is minute relative to the supply of solvent, and the solvent is well mixed, the effective solvent concentration may be assumed constant. Therefore, the rate of dissolution, and rate of change of iron in solution remains constant over the life of the film.

Integrating yields:

$$C(Fe) = kt + C_o(Fe), \text{ where } C_o(Fe) = C(Fe) \text{ @ } t=0$$

The initial iron concentration may be set to zero through the use of reagent grade extractants and distilled water.

Finally, if over the term of thirty plus years of weathering and water rinsing it can be assumed that the contamination (i.e., cesium) has permeated the thin film uniformly, the rate of cesium release can also be modelled as a constant, and the cesium liquid-phase concentration will also follow a straight line with new slope k (pCi/l/s).

B. Resorption

If the concentration of cesium in solution is very low, its rate of increase does not appreciably affect its dissolution rate out of the iron oxide film. However, the loss/gain of cesium in solution will strongly impact the driving force for resorption. As the film is destroyed, new sites are exposed, and other sites previously available but not containing cesium may preferentially sorb the cesium as it is released from the iron oxide. The released atoms may thus cascade from one group of sites (or mechanism) to the next available level of fixation, always sorbing to minimize the energy of the system. Again assuming first order kinetics, the expected rate of resorption for a trace constituent in solution can be modelled as:

$$dC(Cs)/dt = -k'C(Cs)$$

where: $k'$ is the resorption rate constant ($s^{-1}$).

The rate of radioactive decay for cesium with a half-life of 30 years is considered insignificant over the term of the experiments, and is therefore not included above. However, the decay provides a unique opportunity to accurately monitor the concentration in solution at very low concentrations.

Integrating the cesium resorption equation results in a simple exponential decay from an initial liquid-phase concentration:

$$C(Cs) = C_o(Cs)\exp(-k't), \text{ where } C_o(Cs) = C(Cs) \text{ @ } t=0$$

This equation may be used for the period following complete destruction of the iron oxide film, using the cesium concentration for $C_o$ at the point where the iron concentration reaches a constant value. Up to that point, cesium is being constantly released by dissolution and variably resorbed as a function of its solution concentration.

C. Combined Dissolution/Resorption

During dissolution of the iron oxide film, both mechanisms must be considered:

$$dC(Cs)/dt = k - k'C(Cs)$$

Integrating now yields:

$$-1/k'\ln(k-k'C(Cs)) = t + Q, \text{ where } Q \text{ is a constant.}$$

evaluating the integration constant with boundary condition $C_o(Cs) = 0$, results in:

$$C = -(1/k')\ln(k), \text{ or}$$

$$C(Cs) = (k/k')[1-\exp(-k't)]$$

Thus, as resorption becomes increasingly significant (k′ increases), or sufficient time passes, the exponential term approaches zero, and the cesium concentration asymptotically approaches the mathematical ratio between the rate constants for dissolution and resorption. If the constants are in consistent units, the plateau cesium concentration provides an estimate of their relative magnitudes. Thus, under ideal conditions, the time to reach the plateau, the magnitude of the plateau, and the time of decay following dissolution all decrease with increasing

rate of adsorption. This equation is undefined when the resorption rate is zero, and simplifies to the relationship given above for iron. At intermediate values, the cesium profile ranges as shown in Figure 3.1. Cesium concentration increases throughout the duration of the iron-oxide layer dissolution, then resorbs on the residue as long as sites are available.

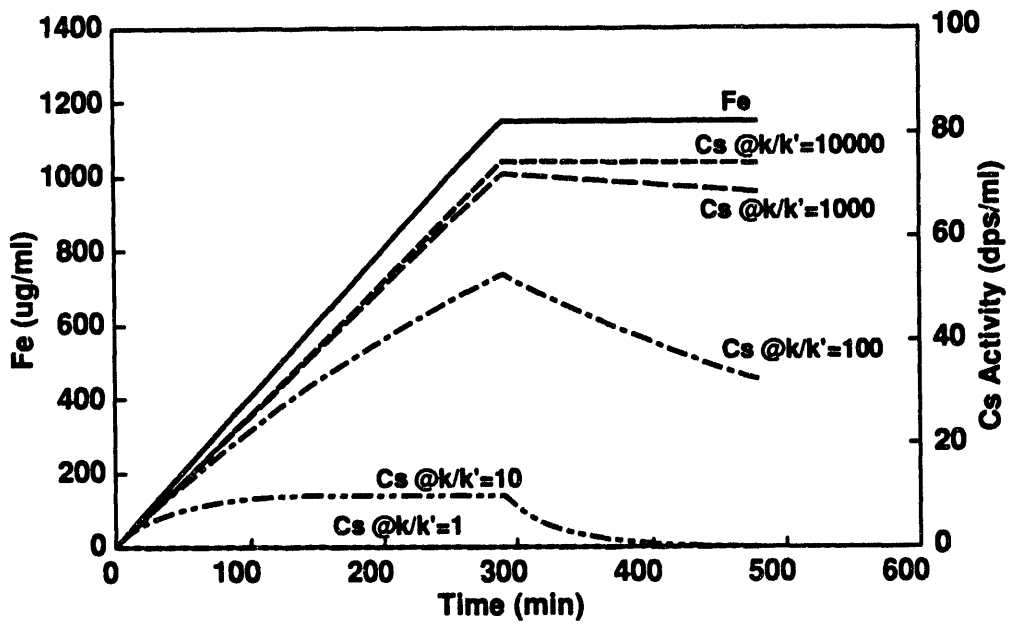


Figure 3.1 Relative Rates of Dissolution (k) vs. Readsorption (k′)
Fe (matrix dissolved) and Cs (contaminant released)

## IV. CONCLUSIONS

The theoretical model provides some understanding of the relative effects of resorption, though from an idealized perspective. It is unlikely that the ideal profiles based on such a simple model (first-order kinetics without competing reactions) would be realized by experimental data. For example, if resorption occurs rapidly, and the sorption capacity is exceeded, the solution analyses will show only a gradual increase to a steady-state value without the predicted peak and decrease following dissolution. The data should, however, demonstrate a significant enhancement in decontamination by using a counter-ion.

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# CHAPTER 4. EXPERIMENTAL DESIGN

## I. INTRODUCTION

This chapter describes an experimental plan for evaluating soil washing technology for potential application to a radioactively contaminated site at the INEL. The experiments were designed at the laboratory screening level in accordance with the EPA guidance documents for conducting treatability studies[1,2] in support of the remedy selection process under the CERCLA.

The experiments planned reflect significant modifications from the procedures in the literature to provide greater insight into the site-specific contaminants at this site. These changes are described under the individual extraction descriptions. The data generated provide the insight necessary to understand the controlling mechanisms which bind contaminants in the soil matrix. A mechanism-specific extractant has the potential for greater removal efficiency than a broad-spectrum extractant, such as acid, while using a less aggressive chemistry and reducing resultant water treatment and dissolved solids handling problems.

## II. TEST OBJECTIVES

The potential for contaminant release using soil washing was characterized by examining the decontamination of a semidesert soil. The sample studied is an prehistoric alluvial sediment deposited by the Big Lost River on the Snake River Plain within the boundaries of the Idaho National Engineering Laboratory (INEL). The INEL is a semidesert, 890 square mile Department of Energy reservation in southeast Idaho, about 32 miles west of Idaho Falls. Annual precipitation is about 9 inches per year. The four-acre Warm Waste Pond (WWP) site at the Test Reactor Area (TRA) consists of three infiltration/evaporation cells contaminated over a period of several decades by the outfall of cooling water containing chromium corrosion inhibitor and trace amounts of radionuclides including cesium. Though

originally thought to be hexavalent chromium, speciation studies have proven essentially all of the chromium to be in the much less soluble trivalent form. The soil is a poorly sorted mixture of volcanic origin, approximately 40 wt% of which is below 4 mesh.

Specific goals are to:

A. Determine the controlling fixation mechanism(s) for Cs, Co, and Cr in the Warm Waste Pond soils.

B. Verify the experimental technique of sequential extraction for selectively attacking fixation mechanisms to provide a basis for evaluating soil washing.

C. Determine the optimum extent of decontamination achievable as a function of soil matrix dissolved.

D. Determine the amount of contamination held in the mineral matrix which represents the absolute limiting values for practical application of soil washing.

E. Evaluate time-release data to determine the relative effects of contaminant resorption on net release.

F. Develop recommendations on the applicability of soil washing technology to the contaminants in the Warm Waste Pond soils.

## III. EXPERIMENTAL DESIGN AND PROCEDURES

### A. Sample Handling

The soil source for these experiments was oxygenated and weathered, hence did not require a controlled atmosphere to minimize oxidation. Humidity control was required after initial homogenization and drying to ensure

consistent sample size between sample replicates and extraction experiments. Contaminants of concern were limited to chromium, cesium, and cobalt, but soil matrix elements including silicon, aluminum, manganese, iron, calcium, and both organic and inorganic carbon were also analyzed, so samples were handled in glass during extractions, and glass or clean disposable non-metallic lab ware for dry samples. The one exception was during wet screening for the initial particle size separation which used stainless steel screens and deionized water. Here after the species listed above are referred to collectively as the analytes.

The following description of the experimental design is illustrated in Figure 4.1.

B. Sample Homogenization and Sizing

Native soil material was wet sieved using deionized water and stainless steel screens of mesh sizes #4, #10, #40, #100, #200 and #400. Sizing continued until approximately one kilogram (dry weight) of -40 mesh material was collected. The percentage of soil in each size fraction was recorded after ambient air drying to remove free liquids. Samples from each size fraction were dried to constant weight at 105°C, to avoid the possibility of modifying the soil matrix chemistry, such as removing waters of hydration from hydrated metal oxide films.[3] After drying, the soil fractions were kept in air-tight containers to minimize the amount of moisture readsorption.

Water was continuously sprayed over the top screen and recycled from the bottom pan during screening. Samples of the water were taken before and after screening to be analyzed for radioactivity, chlorides, sodium, potassium and the analytes to check for washing effects during sizing. An after-screening sample was taken directly from the reservoir containing the screening rinsate, or if more than one batch was necessary, composited from individual batches.

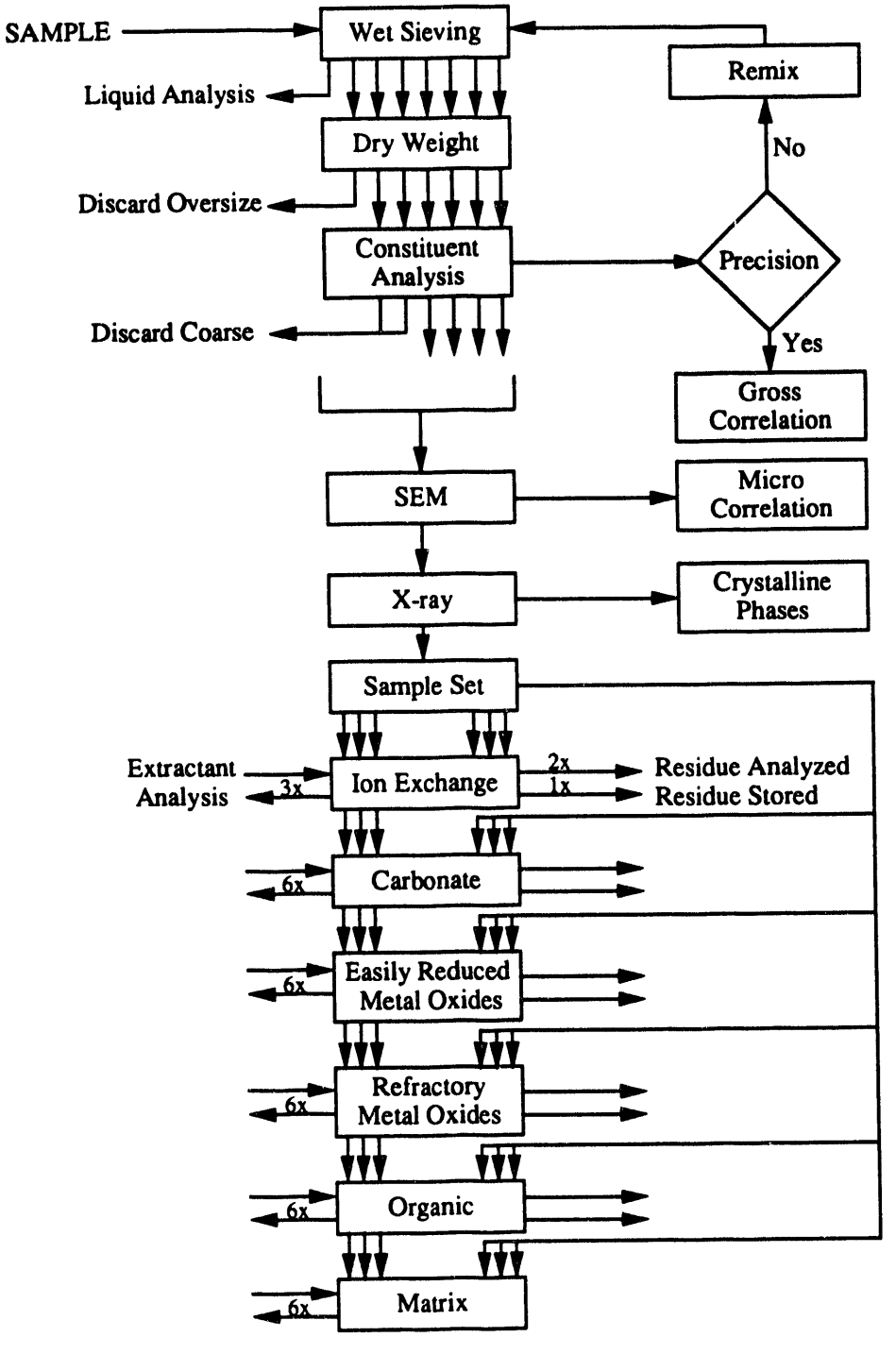


Figure 4.1 Experimental Design Flowsheet.

## C. Sample Preparation and Preliminary Analyses

Triplicate samples of each soil size fraction smaller than 4 mesh (six fractions) were chemically analyzed to determine the analyte content of each fraction. This data provided insight into any correlation of the contaminants of concern with gross soil matrix chemical constituents. The triplicate samples also provided insight into the homogeneity of the initial sample. The material was to be remixed if the precision of the chemical analyses across the triplicates was not within ±20%. Based on prior studies,[4,5] which indicated the pond soils are virtually all either +65 mesh or -200 mesh, the size fractions were then combined into +40 and -40 mesh sizes to simplify handling for the extractions. Based on the assumption that any effective extraction scheme developed for the fine material would be at least as effective for the coarse material, the balance of the experiments was conducted using the -40 mesh fraction only.

Scanning electron microscopy (SEM) analyses were done to provide representative elemental maps for each analyte and selected soil matrix constituents to determine if the contaminants of concern could be correlated with any trace chemical constituent or surface phenomena. "Representative" was determined by examining several surface sites of several particle sizes and appearances, but only sites showing distinct characteristics were recorded photographically.

X-ray diffraction was done in a similar explorative manner to determine what the major crystalline phases were and if the contaminants could be correlated with any dominant phase.

## D. Chemical Extractions

Thirty (30) samples of about one gram each (1±0.1 g) of the -40 mesh material were weighed out and stored in air tight containers with minimal head space for use in the extractions.

## 1. Extractants

All solutions were made using deionized water and analytical grade reagents. Liquid samples taken before and after the extractions were analyzed for the added reagents as well as for pH and the experimental analytes. All extractions were continuously shaken, and conducted at room temperature unless otherwise indicated, and the temperatures were monitored. The extractants were then centrifuged, and the solid residues were rinsed twice with 5 ml of deionized water. The rinsates were combined with the extractants. After-extraction, liquid analyses were done on this combined solution. The solid residues were air dried, weighed, and stored in air-tight labeled containers. Each extraction treated samples subjected to prior extractants as well as fresh samples to determine how the soil matrix changes caused by one treatment affected later treatments.

## 2. Exchangeable Phase

Six one-gram samples were each extracted using 20 ml of 1 M potassium nitrate solution at pH 7 and room temperature, shaken for 2 hours. Potassium nitrate was used over magnesium chloride to avoid the potential for precipitation of magnesium carbonate. Ammonium acetate was not used to avoid potential for complexing of soil calcium by the acetate.[6]

Potassium was chosen as the displacing cation because it is the next in size to the cesium ion, which should increase the probability for effective ion exchange.[7] Though it has been reported that desorption of cesium from humic materials may not be strictly a function of ion size,[8] it is well known that potassium is virtually the perfect size to fit into montmorillonite 2:1 clay types.[9] As such, it probably provides the greatest likelihood for displacement of cesium from between clay layers. More detail is included below in the discussion on resorption.

All extractants were filtered as described above. Samples of three clear solutions were sampled for the analyte group and sodium, potassium, chloride and nitrate. The solid residue from each extraction was handled as follows:

a) One sample was analyzed for potassium and the analytes to confirm the liquid analyses,
b) Three samples were used in the following extractions, and
c) Two samples were saved in air-tight containers for additional surface analysis if required.

3. Precipitated Salts (Carbonate Phase)

Three new one-gram samples and the three samples from above were extracted using 20 ml of 1 M sodium acetate reduced to pH 5 with acetic acid. The extraction was shaken and maintained at room temperature for 5 hours. The pH was checked each hour and adjusted to pH 5 using acetic acid if drift was over 0.5 pH units. Though some nonselective attack on transition metals in metal oxide coatings and the organic phase is reported in the literature,[10] it was believed that close control of the solution to maintain pH $\geq$ 5 would maintain the desired selectivity.[5] The three samples exposed in both extractions were filtered, all leachates were analyzed for the analytes, and the residue saved for the next step. The three new samples were filtered, the leachates and one residue sample analyzed for the analytes, and the other two residue samples saved in air-tight containers. Extraction leachates and residues from steps 4, 5, 6, and 7 were handled in the same manner.

4. Easily Reducible Phase

Three new one-gram samples and the three samples from above were extracted using 20 ml of 0.1 M hydroxylamine hydrochloride acidified to pH 2 with 0.01 M nitric acid. The extraction was shaken and

maintained at room temperature for 3 hours. This extractant has been proven to be quite selective for manganese oxide phases because its reducing character causes little or no attack on crystallized iron oxides or organic materials.[11,12] The pH was checked each hour and adjusted to pH 2 using nitric acid if drift was over 0.5 pH units.

5. Moderately Reducible Phase

Three new one-gram samples and the three samples from above were extracted using 20 ml of 0.2 M ammonium oxalate acidified to pH 3 with 0.2 M oxalic acid. The extraction was shaken and maintained at room temperature for 6 hours. The pH was checked each hour and adjusted to pH 3 using oxalic acid if drift was over 0.5 pH units.

6. Organic Phase

Three new one-gram samples and the three samples from above were extracted using 15 ml of 30% hydrogen peroxide acidified to pH 2 with 0.01 M nitric acid. The extraction was shaken and maintained at 85°C for 4 hours. The pH was checked each hour and adjusted to pH 2 using nitric acid if drift was over 0.5 pH units. After cooling, 5 ml of 3 M potassium nitrate acidified to pH 2 with 0.01 M nitric acid was added, and the extraction shaken for 30 minutes. The addition of potassium nitrate acted to prevent resorption of freed contaminants on the solid residue. Use of potassium nitrate rather than ammonium acetate was a deviation from the method typically used,[13] to allow analysis for organic carbon in the solid residue to verify complete oxidation of the organic matrix during the heated digestion.

7. Lattice

Three new one-gram samples and the three samples from above were digested using 20 ml of a 3/1 mixture of concentrated hydrochloric and nitric acids at 85°C until no solids were visible. More acid was

added as required to attain complete digestion if residue remained after 1 hour. Hydrofluoric acid was added drop-wise to attain complete dissolution.

## IV. TIME RELEASE STUDIES

To make engineering use of the sequential extraction data, the release of contamination must be isolated from the effects of resorption. Either adsorption on identical virgin soil can be monitored such that rate and magnitude can be quantified directly, or a means must be demonstrated to maintain the extracted species in solution, minimizing the mass action driving force for resorption. This simplistic goal is made more challenging by the heterogeneity of natural materials such as soil and the complexities of the soil matrix. Grinding the soil, using only a narrow particle size fraction, or any other technique which might normally be used with synthetic resins or catalysts to isolate specific physical phenomena, will modify the characteristics of the native soil matrix invalidating the experiment.

Evaluating release and desorption phenomena separately for the same soil requires releasing the contaminant without allowing it to resorb by displacing another ion sorbed at lower energy. This can be accomplished using an ion of greater adsorption affinity for the substrate or by concentration (as in ion exchange regeneration) or both. Potassium was chosen as the displacing ion because its size, charge, and chemistry yield the greatest potential for mitigating resorption at even sterically hindered sites inside silicate structures.[7,9,14,15]

Based on this principle, rate studies were conducted to qualitatively determine the significance of resorption versus dissolution and contaminant release. For example, as the moderately-reducible metal-oxide fraction of the soil matrix (characterized mainly by crystalline oxides of iron) was destroyed in the sequential extraction, the concentration of iron, chromium, and the cesium activity in solution were monitored and evaluated

based on the model described in Chapter 3. The occurrence of a radionuclide with a high-energy decay allowed very sensitive measurement of contaminant release over time. The relative shapes of the profiles were then compared for extractions with and without the presence of a strong potassium nitrate brine present to mitigate the resorption of cesium. Similar studies were done for the extractions to destroy the carbonate and easily-reducible metal oxide phases by monitoring calcium and manganese respectively.

The brine can change the apparent contaminant distribution in two ways: 1) by mitigating resorption of the released species, or 2) by mass-action causing potassium to actively displace sorbed ions thereby enhancing the release. Practically, both effects will occur at sites made available to the solution during dissolution, but misleading data could result if the potassium actually penetrates into the surface to displace contamination from a phase not attacked by the extractant. This would again result in a faulty estimation of contaminant distribution. To minimize this potential all time-release samples were pretreated with brine to displace all available cesium prior to conducting the time-release extractions.

## V. EQUIPMENT

A. Fritsch A-3 Vibratory Sieve Shaker equipped for wet screening, and stainless steel screen sizes: #4, #10, #40, #100, #200, and #400.

B. Cole-Parmer temperature-controlled water bath horizontal shaker and stainless steel tank.

C. DIONEX Ion Chromatograph(IC) (DIONEX series 4500i)

D. Inductively Coupled Plasma(ICP) Sequential Spectrometer SN AVRIL 83/387 (ISA JY-38)

E. Flame Atomic Absorption(AA) Spectrophotometer Thermo Jarrell Ash (Smith Hieftje model 4000 S#8128)

F. Gamma Spectrometer System

G. $CO_2$ Coulometer (UIC Inc. model 5011)

H. Carbonate System (UIC Inc. model 5130)

## VI. ANALYTICAL METHODS

Summarized in Table 4.1 are all analytes, analytical methods, and, where available, corresponding EPA standard methods.

### A. Inductively Coupled Plasma (ICP)

Compounds are broken down to elements in a high-temperature plasma. The excited elements give off light at characteristic frequencies which are resolved by a detector.

### B. Atomic Absorption (AA)

The compounds to be analyzed are atomized into a flame in the path of a light source of a specific wavelength. The wavelength is chosen for the specific element of interest to be absorbed in a quantum interaction. The degree of absorption can be resolved to quantify the amount of the element present in the sample.

### C. Gamma Scan

Gamma ($\gamma$) rays (photons from nuclear decay) incident on a germanium crystal yield free electrons in amounts proportional to the absorbed energy. Due to an imposed voltage on the crystal, a current profile is produced as a function of photon energy and frequency of impact. Detector software is

| Table 4.1 Analytical Methods | | |
|---|---|---|
| Analyte | Technique | Standard Method |
| Cr | ICP | SW-846; 6010A |
| Si | ICP | |
| Al | ICP | SW-846; 6010A |
| Mn | ICP | SW-846; 6010A |
| Fe | ICP | SW-846; 6010A |
| Ca | ICP | SW-846; 6010A |
| Na | AA | SW-846; 7770 |
| K | AA | SW-846; 7610 |
| $Cs^{137}$ $Co^{60}$ | Gamma Scan | No EPA method |
| $NO_3$ | IC | 9056; EPA-600 Method 300 |
| Cl | IC | 9056; EPA-600 method 300 |
| Inorganic C | | ASTM D4129-82 |
| Total C | | ASTM D513-82 |
| Density | | Helium Displacement |
| Surface Mapping | | Scanning Electron Microscopy |

capable of resolving up to $10^6$ impacts per second to produce a spectrum of photon incidence versus energy. Nuclide prevalence can then be determined by the size of the peak at characteristic energies.

D. Ion-chromatography (IC)

Nitrate and chloride were separated by ion-chromatography as described in

Chapter 3, then titrated as acids.

E. Inorganic/Organic Carbon

To measure inorganic carbon, the sample is heated to convert carbonate to carbon dioxide which is captured for titration as carbonic acid. For total carbon, the sample is heated to a higher temperature to not only convert the carbonate but to burn the organic carbon as well. Organic carbon is determined by difference.

F. Density by Helium Displacement

The sample is contained in a cylinder of precisely known volume with a helium atmosphere. The cylinder is repeatedly pressurized by displacement with a piston. Pressure increase versus volume is interpreted to determine the exact volume of the sample exclusive of pore spaces filled by the helium. Combined with a weight determination, the absolute density of the particle may be calculated

G. Scanning Electron Microscopy

A narrowly focused electron beam is used to bombard a small portion of the sample surface in scanning electron microscopy (SEM). Incident electrons are either reflected from the surface, or penetrate to ionize surface atoms. Incident electrons are of essentially identical energy, but reflected electron energies are distributed across a spectrum because each recoil causes a certain loss characteristic of the surface atom. Thus the reflected electrons (backscatter) can be sorted by energy to derive the elemental composition of the surface (electron dispersive spectroscopy or EDS). The EDS spectrum provides information on the relative incidence of elements occurring at the surface to at least 0.1% atomic prevalence. The backscatter electrons can also be mapped: generally to provide a topographical image (backscatter electron imaging or BEI), or at a single energy to provide a "dot map" showing the incidence of a single element.

Penetrating electrons can ionize surface atoms causing a high-energy photon emission (x-ray) and loss of an electron from an outer orbital (secondary electrons). Secondary electrons are produced over a narrower range of energies because they are limited to quantum energies lower than the incident electrons and are not affected by surface geometry. This makes secondary electron imaging (SEI) more valuable to produce topographical maps with higher contrast.

## VII. DATA ANALYSIS AND INTERPRETATION

The extraction efficiency (degree of contaminant removal) was measured by gamma scan and chromium analysis of the extractant and the soil residue. Specificity (attack on only the target compound), and completeness (degree of target compound removed) was evaluated, as applicable, for each step as follows:

### A. Exchangeable Phase

All contamination removed in this step should be the result of potassium displacement at ion exchange sites. Potassium removal from the extractant was compared on an equivalent basis to the cation addition to evaluate specificity. Analysis of the soil residue was compared to match the potassium pickup versus the loss of other cations. Detection of calcium, aluminum, iron, or manganese could indicate attack on carbonate or hydrated oxide fractions, but could only be due to ion exchange interactions. Loss of inorganic carbon or silicon from the solids would indicate attack on the carbonate fraction or mineral lattice respectively.

### B. Precipitated Salts (Carbonate Phase)

Contaminant removal in this step should be due to dissolution of carbonates which may precipitate or occlude the ions of concern. For example, cesium does not form an insoluble carbonate, but may be trapped in a pore which is blocked by an insoluble cobalt carbonate. Calcium addition to the

extractant, and inorganic carbon analysis of the solid residue was used to judge the completeness of the carbonate dissolution. Presence in the extractant of aluminum, iron, manganese, or silicon would indicate lack of specificity.

C. Easily Reducible Phase

This step should primarily remove hydrated oxides of manganese and amorphous iron oxides. It will also remove any residual carbonates. Completeness of reaction was to be evaluated by measuring residual manganese in the solid residue. Silicon in solution, or loss of organic carbon from the solids would indicate lack of specificity.

D. Moderately Reducible Phase

This step should remove the remaining more refractory iron oxides. The hydrated oxides are removed in two steps to determine how much contamination can be liberated by dissolving the least amount of soil matrix. Completeness of reaction was to be evaluated by measuring residual iron and manganese in the solid residue. Silicon in solution, or loss of organic carbon from the solids would indicate lack of specificity.

E. Organic Phase

This step should oxidize essentially all of the organic materials. The extraction could use more aggressive chemistry to ensure complete oxidation, but this method was chosen as a compromise to prevent significant attack on the mineral lattice.

Completeness of reaction was evaluated by measuring residual carbon in the solid residue. Silicon in solution would indicate attack on the mineral lattice and lack of specificity.

F. Lattice

This final digestion of the remaining solid matrix released residual contaminants trapped in the silicate matrix. Contaminants remaining in this solution provided a mass balance on the earlier extractions, and an indication of the limiting concentrations that could be reached by practical applications of soil washing technology. Removal of the contaminants held within the silicate matrix is not believed possible by any practical field application of soil washing technology.

## VIII. CONCLUSIONS

This experimental plan represents not only a comprehensive evaluation of a technology for a specific application, but the basis for understanding how a remediation technique works. Rather than a simplistic positive/negative result which is typically all that is allowed due to economic constraints, this type of plan provides the data on which to base a true engineering systems approach. A knowledge base is established including: 1) which mechanism(s) should be targeted by a flowsheet, 2) how aggressive a chemistry will be required, 3) how much dissolved solid must be treated, and 4) what degree of decontamination can be expected from the technology. The final assessment of remedies can then be explained in a manner acceptable to the public which will build credibility and confidence through shared knowledge.

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# CHAPTER 5. EVALUATION

## I. INTRODUCTION

This chapter covers the findings of the experimental plan outlined in Chapter 4. The study was reviewed and approved by the Department of Energy, Region 10 of the Environmental Protection Agency, and the State of Idaho, Department of Health & Welfare. At the time of this study, Fall, 1992, the Warm Waste Pond at the Test Reactor Area was subject to a CERCLA Record of Decision[1] (ROD) agreed to by these three organizations, which prescribed soil washing to decontaminate the pond sediments. The ROD included cleanup goals of 90% removal of total contamination and an average residual cesium concentration of 690 pCi/g. At the time the document was written, the chromium was known to be trivalent, so no residual level was specified other than the general 90% criterion. Many experiments had been done which suggested application of this technology might not reach these goals, but no definitive data were available to change the agreement. This evaluation contributed to the decision to seek an alternative solution, such as physical separation and/or capping.

## II. SOIL CHARACTERIZATION

### A. Particle Size Distribution

Three soil samples from the Warm Waste Pond were blended together in their entirety and wet-sieved using distilled water and No. 4, 10, 40, 100, 200, and 400 ASTM standard sieves. This provided nominal particle size cuts of: 4.75 mm, 2 mm, 425 $\mu$m, 150 $\mu$m, 75 $\mu$m, 38 $\mu$m and fines respectively. The sieve stack is shown in Figure 5.1. The stack is shaken, and water is distributed via spray heads over the solid sample on the top screen to promote breakup of agglomerates and rinse fine material down through the sieves. The rinse water is centrifuged to recover the material smaller than 38 $\mu$m.

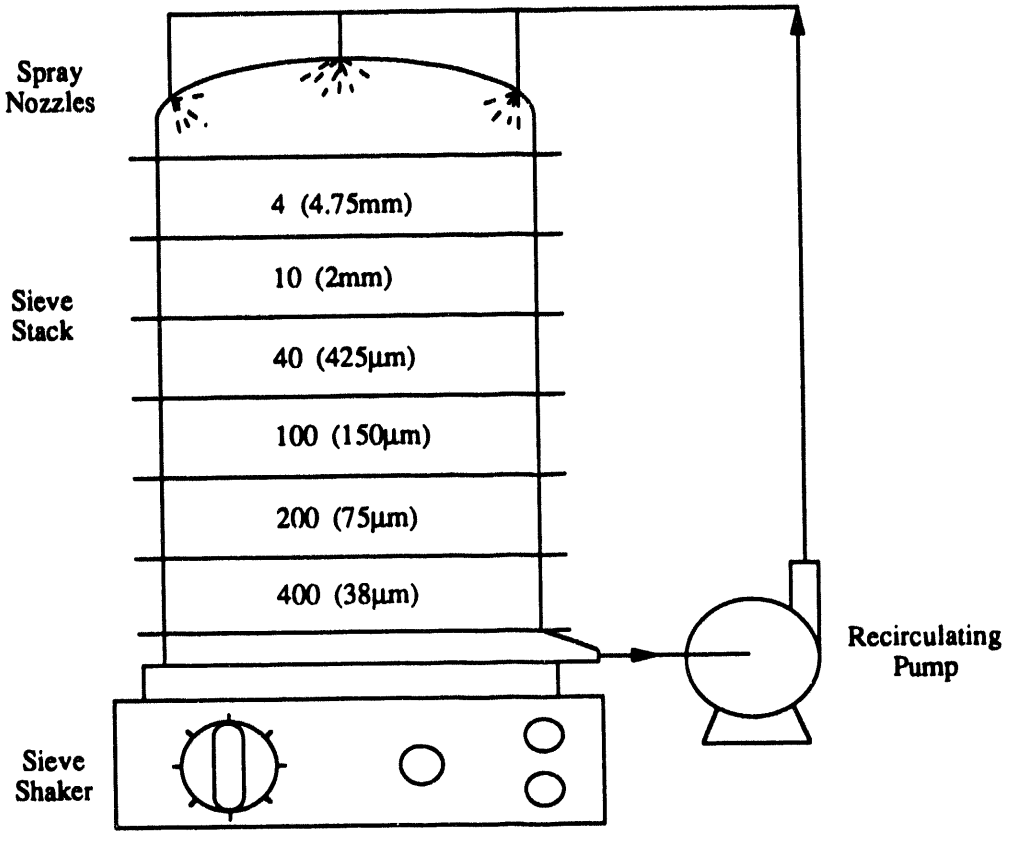



Figure 5.1 Particle Size Classification Sieve Stack.

The material was received moist, but significant rinse water had to be added in the sieving process to avoid agglomeration and attain good separation of the particles. The initial sieve fractions were then resieved repeatedly to ensure maximum separation and minimal physical contamination of the larger material with fines that were suspected to carry significant concentrations of chemically-bound species of concern. The sieving operation was kept as gentle as possible to minimize attrition and damage to the as-received particle surfaces. This procedure significantly increased the time to complete sieving, but is believed

justified by ensuring the most reproducible and representative results. Approximately one liter of distilled water was used to sieve a total of 28,892 grams of soil. Analysis of the rinse indicated negligible losses of

any of the monitored analytes (less than 0.1%), with the exception of organic carbon which lost about 0.5 wt%, probably as colloidal material. About 0.05% of the cobalt activity was found in the rinsate with about two orders of magnitude less effect on the cesium or chromium.

The particle size fractions were then air dried and weighed. The resultant distribution is given by weight fraction in Table 5.1 and Figure 5.2. As can be seen in Figure 5.3, over two thirds of the material is greater than 10 mesh, and about 85 wt% of the material is over 40 mesh. This

Table 5.1 Soil Size Distribution

| Sieve Size | Screen Opening $\mu m$ | Average Diameter $\mu m$ | Weight Fraction Wt. % | Particle Specific Gravity | Relative Surface Area $A/A_{10}$ |
|---|---|---|---|---|---|
| +4 | 4750 | ---- | 59 | ---- | ---- |
| +10 | 2000 | 3375 | 12 | 2.66 | 1.0 |
| +40 | 425 | 1212 | 14 | 2.65 | 2.8 |
| +100 | 150 | 287 | 7.4 | 2.62 | 11.9 |
| +200 | 75 | 112 | 2.0 | 2.58 | 30.9 |
| +400 | 38 | 56 | 1.6 | 2.56 | 61.9 |
| -400 | 38 | ---- | 3.9 | 2.56 | ---- |

distribution provides an opportunity for segregation of the bulk of the material by simple screening. If a decontamination flowsheet is proven effective for the finer material, a modified, or possibly less intense treatment may then suffice for the large material.

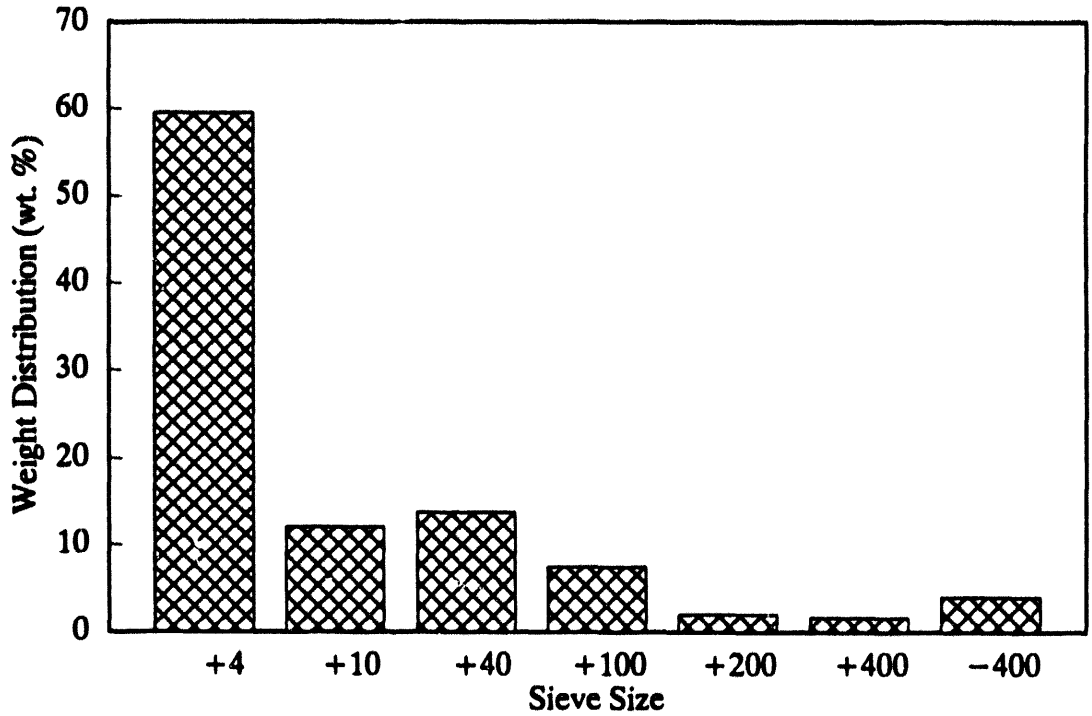



Figure 5.2 Weight Percent by Size Fraction.

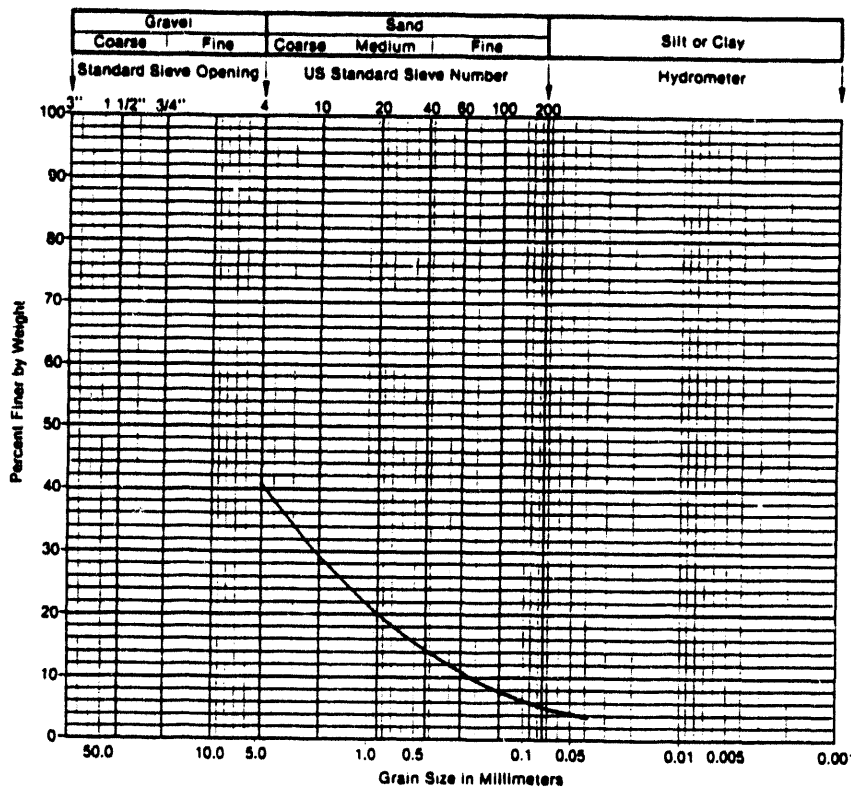



Figure 5.3 Particle Size Distribution (% finer than).

B. Radionuclide Distribution

Incidence of radioactive cesium and cobalt as measured by $\gamma$-scan is summarized by particle size in Figure 5.4. As can be seen, both species increase monotonically with decreasing particle size. Though not apparent in the figure due to the magnitude of the cesium contamination, cobalt is present in all size fractions. Numerical values are listed in Table 5.2. It may also be seen in the table that none of the size fractions meet the criterion in the Record of Decision of 690 pCi/g for allowable residual contamination.

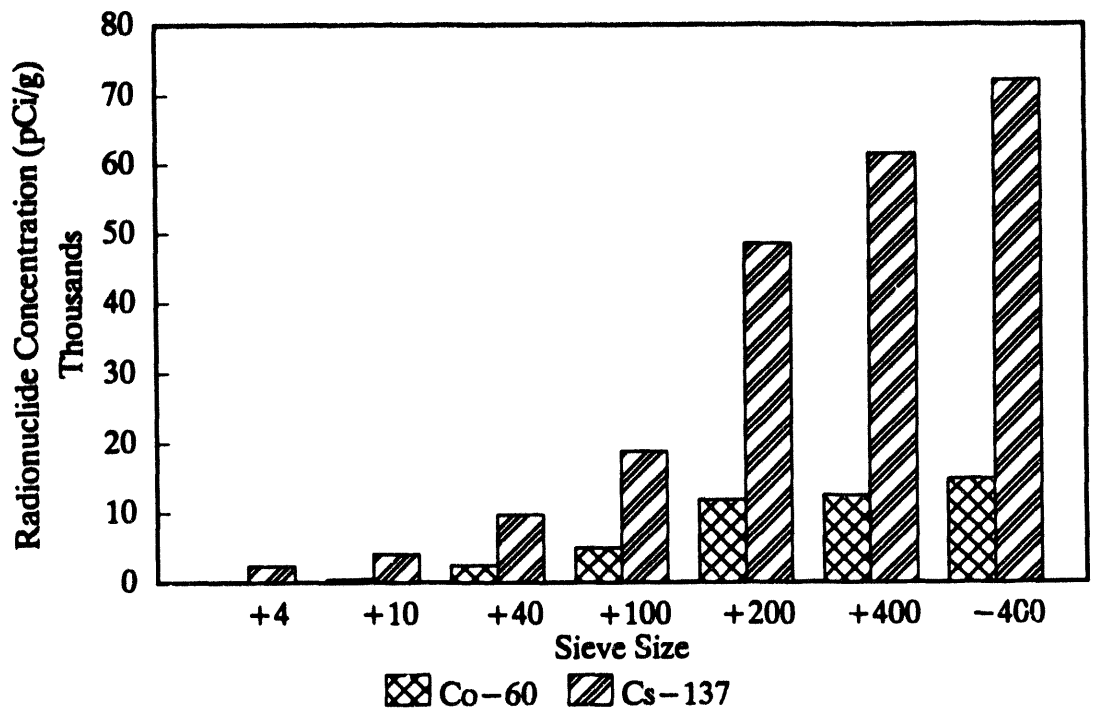



Figure 5.4 Radionuclide Incidence by Size Fraction.

The ratio of cesium to cobalt decreases from over 30 in the largest size fraction to about five in the fines. This suggests different dominant fixation mechanism(s) for the two radionuclides, as might be expected based on their different positions in the periodic table. Cesium is an alkali metal and distributes in a manner similar to potassium, its nearest

chemical and physical analogue, and naturally occurring soil matrix constituent. Cobalt is a transition metal, and as such distributes primarily with iron and manganese, both of which are also naturally occurring.

Table 5.2 Radionuclide Distribution

| Sieve Size | $Co^{60}$ (dps/g) | $Co^{60}$ (pCi/g) | $Cs^{137}$ (dps/g) | $Cs^{137}$ (pCi/g) |
|---|---|---|---|---|
| +4 | 2.7E+00 | 7.2E+01 | 8.8E+01 | 2.4E+03 |
| +10 | 1.4E+01 | 3.8E+02 | 1.5E+02 | 4.1E+03 |
| +40 | 8.8E+01 | 2.4E+03 | 3.6E+02 | 9.7E+03 |
| +100 | 1.8E+02 | 5.0E+03 | 7.0E+02 | 1.9E+04 |
| +200 | 4.4E+02 | 1.2E+04 | 1.8E+03 | 4.9E+04 |
| +400 | 4.6E+02 | 1.3E+04 | 2.3E+03 | 6.1E+04 |
| -400 | 5.5E+02 | 1.5E+04 | 2.7E+03 | 7.2E+04 |

When coupled with the particle size distribution, it can be seen that only about one-third of the total activity occurs in the 85 wt% larger than 40 mesh, and two-thirds is incident in the remaining 15 wt% (Figure 5.5). This reinforces the potential for screening to separate the most contaminated 15 wt% for treatment, with a simplified flowsheet for the larger material.

C. Elemental Distribution

The soil fractions were analyzed for the seven primary matrix constituents to be tracked in the sequential extractions: silicon, aluminum, calcium, iron, manganese, and inorganic and organic carbon, and the only nonradioactive contaminant of concern, chromium. The standard deviation for triplicate samples taken as a percentage of the average value ranged from 1.2 to 21%. Of the 36 triplicate sets, only two values exceeded the 20% criteria in the experimental plan, so no further mixing was warranted. The triplicate data is summarized in Appendix A. The average values of the

elemental concentrations are listed in Table 5.3.

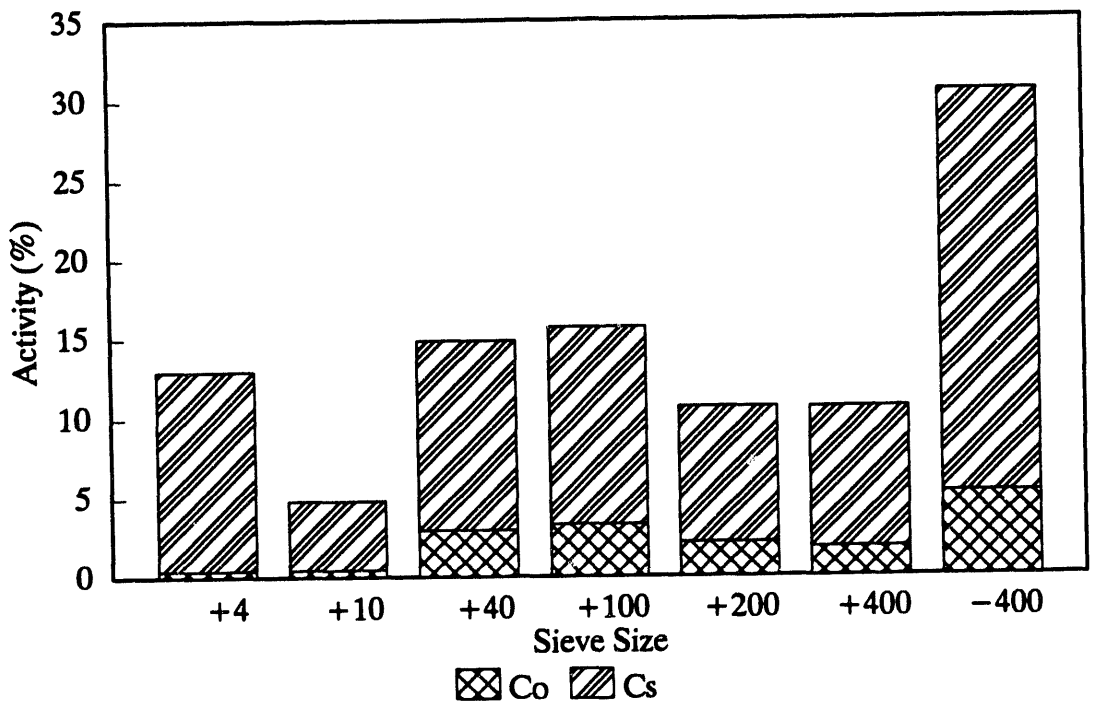



Figure 5.5 Total % Activity by Size Fraction.

Table 5.3 Elemental Distribution by Particle Size

| Sieve Size | Elemental Wt% | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Al | Fe | Cr | Si | Mn | Ca | C-$CO_3$ | C-Org |
| +4 | <----------No Representative Sample----------> | | | | | | | |
| +10 | 3.88 | 1.24 | 0.02 | 31.13 | 0.02 | 2.45 | 0.61 | 0.23 |
| +40 | 4.75 | 1.63 | 0.07 | 31.10 | 0.04 | 1.00 | 0.06 | 0.70 |
| +100 | 4.79 | 1.70 | 0.13 | 30.47 | 0.05 | 1.44 | 0.12 | 1.46 |
| +200 | 3.70 | 2.65 | 0.35 | 23.40 | 0.13 | 3.24 | 0.67 | 3.19 |
| +400 | 4.98 | 2.60 | 0.37 | 25.97 | 0.13 | 3.13 | 0.49 | 3.88 |
| -400 | 4.67 | 3.01 | 0.63 | 22.47 | 0.20 | 2.16 | 0.37 | 4.14 |

This data is also summarized in Figures 5.6 and 5.7. The second figure magnifies the minor constituents by removal of the dominant silicon and

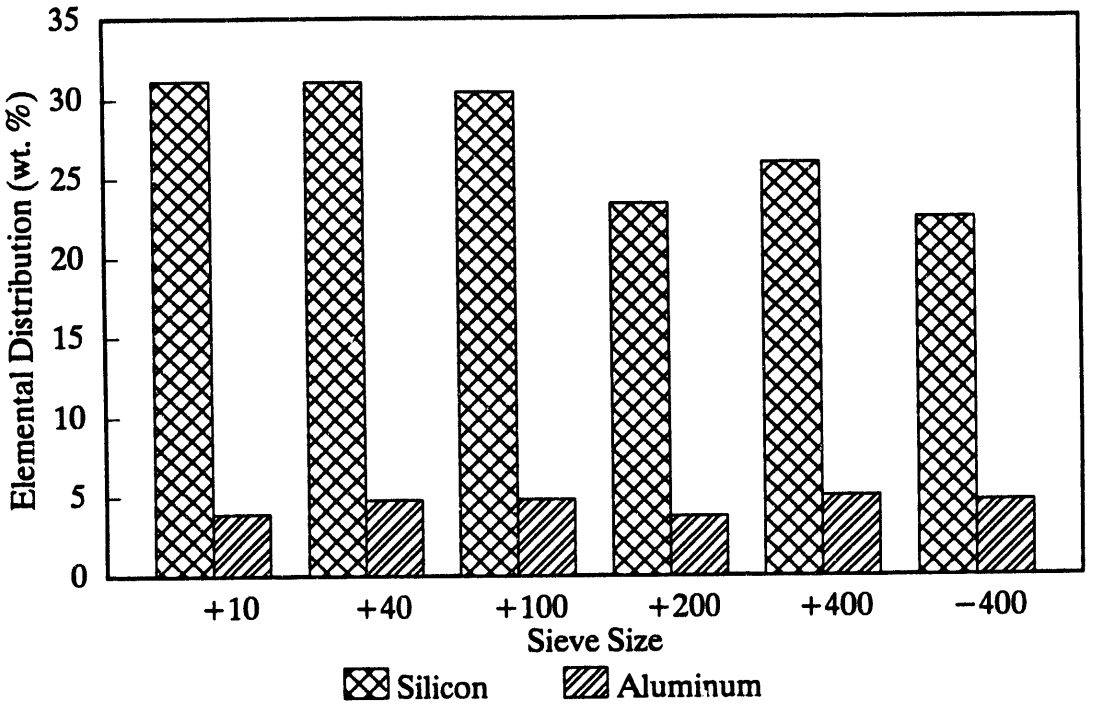



Figure 5.6 Matrix Si and Al Distribution by Particle Size.

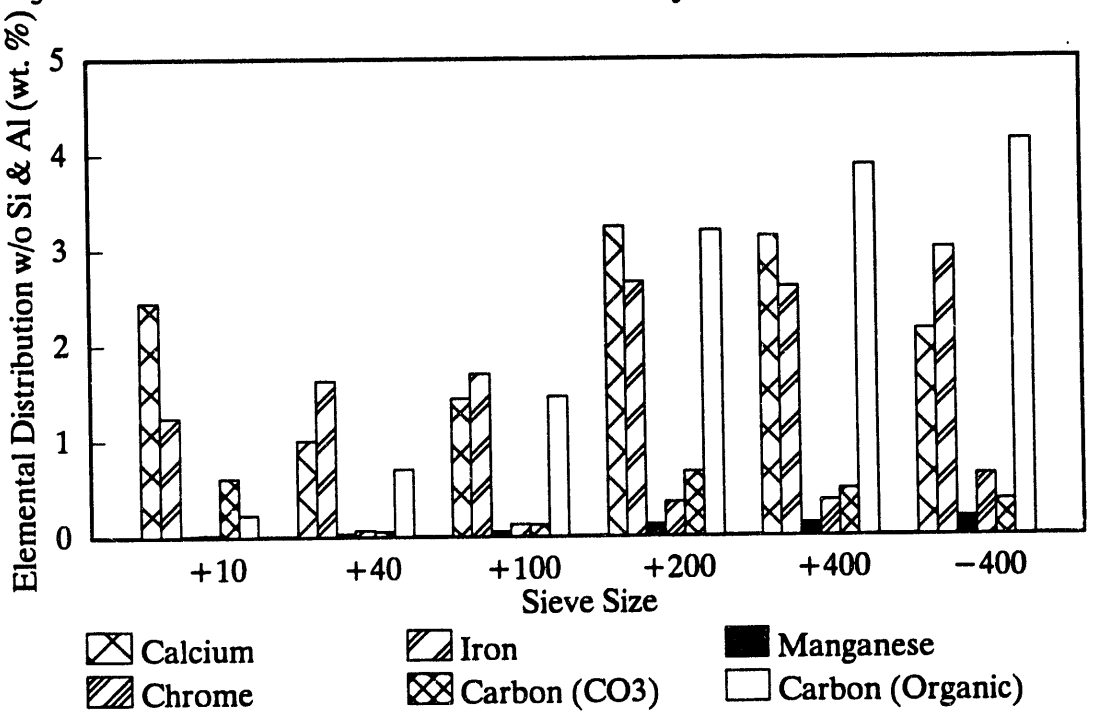



Figure 5.7 Elemental Distribution by Particle Size Minor Matrix Elements w/o Si & Al.

aluminum bars. As can be seen, the iron, manganese, chromium and organic carbon values all show a general increase with decreasing particle size, with profiles similar to the radionuclide distribution shown above.

Also in Table 5.1 are the absolute particle densities as measured by helium displacement. The surface areas estimated in the table are based on the particle densities and the assumption that the particles are essentially solid mineral grains with minimal porosity. This assumption is supported by at least one historical microscopic examination of INEL soils,[2] and the results of the scanning electron microscopy described below. If the particles are essentially convex solids, surface area is proportional to the square of a characteristic diameter, and mass is proportional to the product of density and the cube of a characteristic diameter. For example, specific surface area ($cm^2/g$) of a spherical particle is related to diameter and density as:

$$\text{Specific Surface Area } (cm^2/g) = (4\pi r^2)/(\rho 4\pi r^3/3) = 3/r\rho$$

The derivation for any fairly uniform particle yields the same result, so the particular cleavage of any specific mineral lattice is irrelevant. Therefore, plots of contaminant distribution versus the inverse of the product of average particle radius and density should give a linear plot to the extent that the contamination is physically and not chemically distributed. Figures 5.8-5.14 are plots of incidence of contamination versus surface area or a soil matrix constituent. Normalizing the surface area, elemental, and activity data for all particle sizes to the values for the +4-10 mesh material, make the scales comparable, illustrating only the change in one parameter versus another. As can be seen from Figure 5.8, the contaminants do not distribute solely due to surface area as would an inert coating such as paint. In fact the distribution falls below the theoretical curve based on surface area alone, which indicates a decreasing contaminant concentration density by available surface. Therefore, there must be some partitioning due to selective interaction with particular elemental or crystalline species.

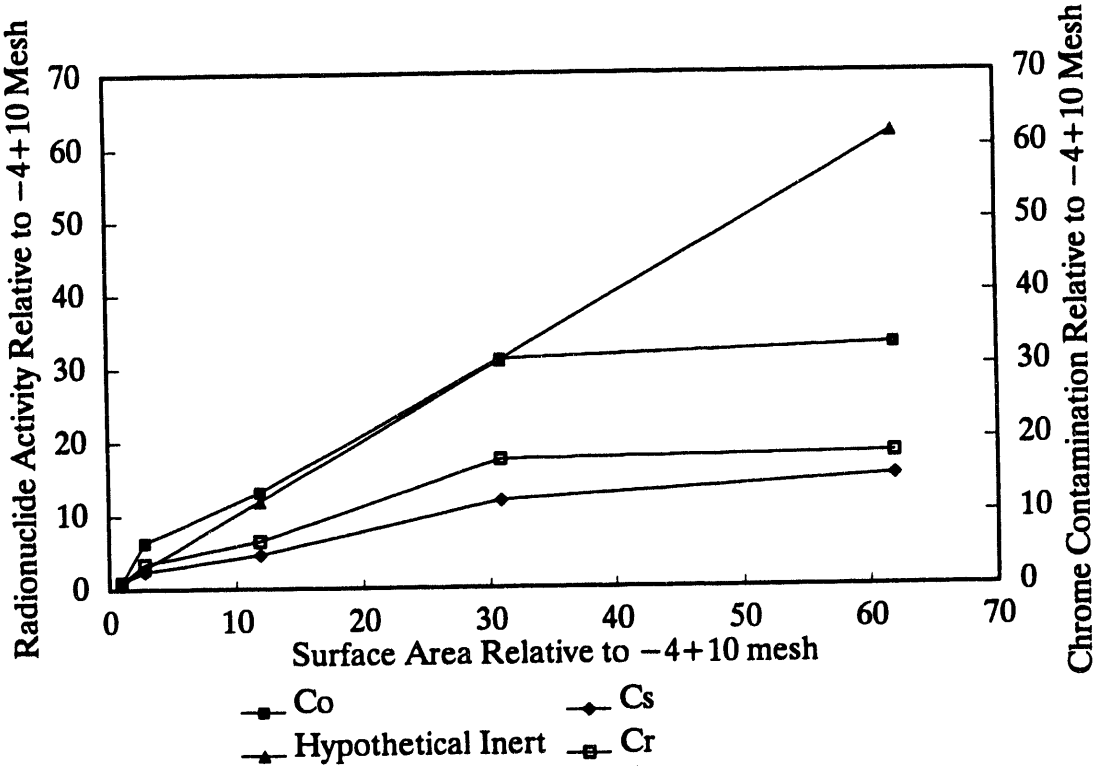



Figure 5.8 Relative Contamination Distribution vs. Surface Area.

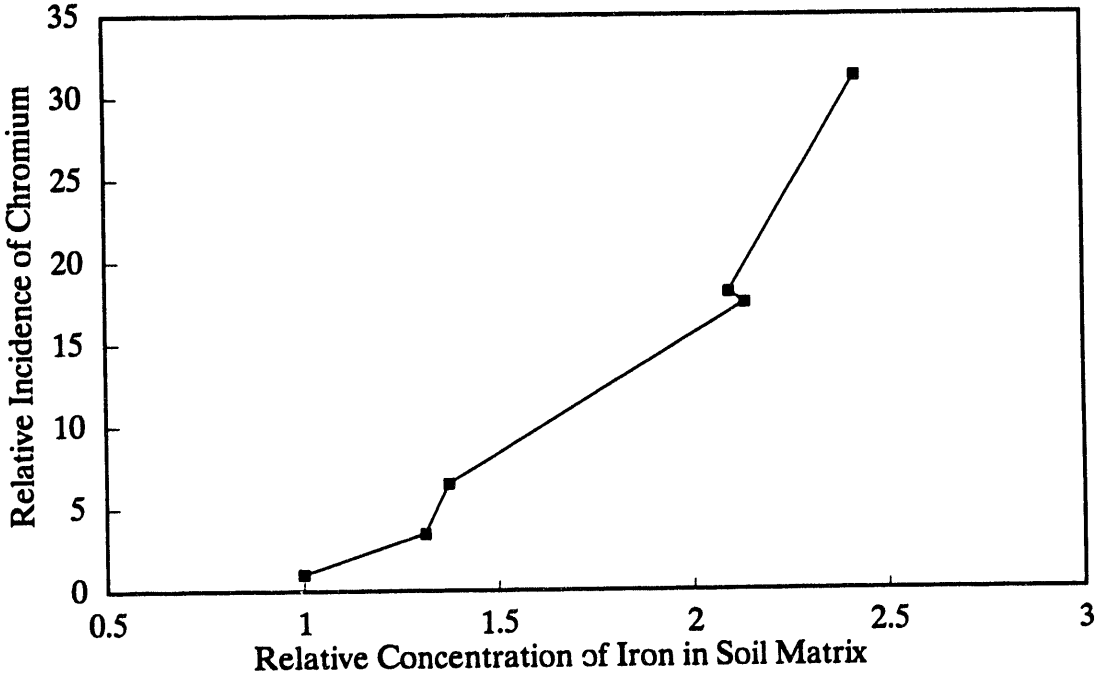



Figure 5.9 Correlation Test of Contamination vs. Soil Constituent, Chromium Distribution vs. Iron in Matrix.

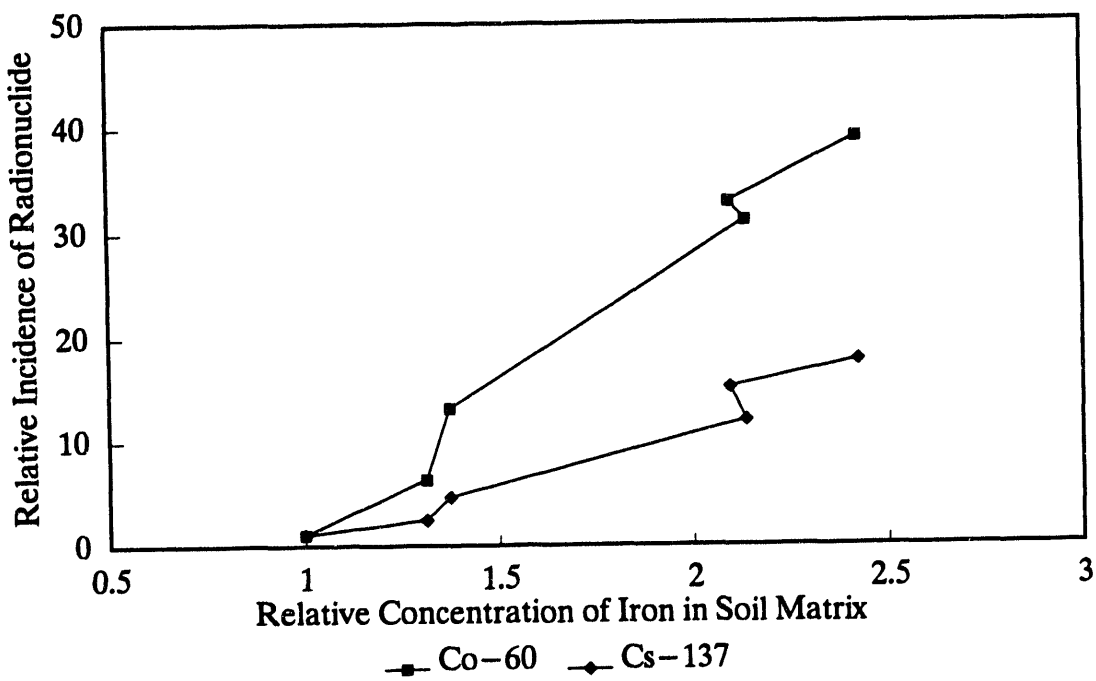



Figure 5.10 Correlation Test of Contamination vs. Soil Constituent, Radionuclide Distribution vs. Iron in Matrix.

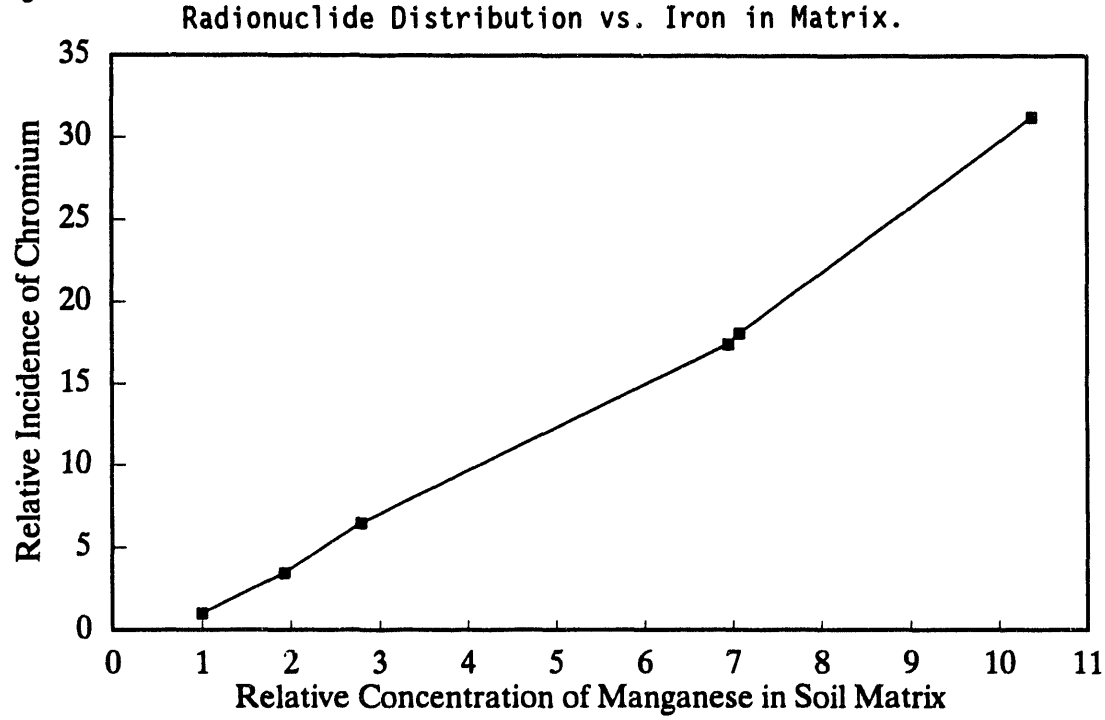



Figure 5.11 Correlation Test of Contamination vs. Soil Constituent, Chromium Distribution vs. Manganese in Matrix.

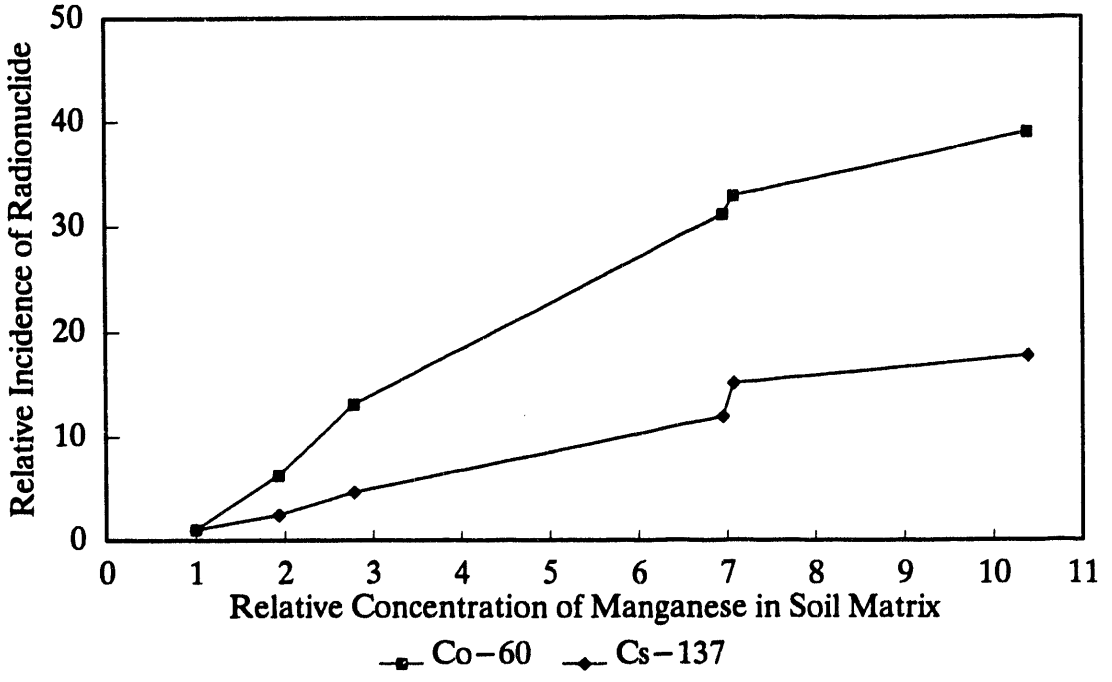



Figure 5.12 Correlation Test of Contamination vs. Soil Constituent, Radionuclide Distribution vs. Manganese in Matrix.

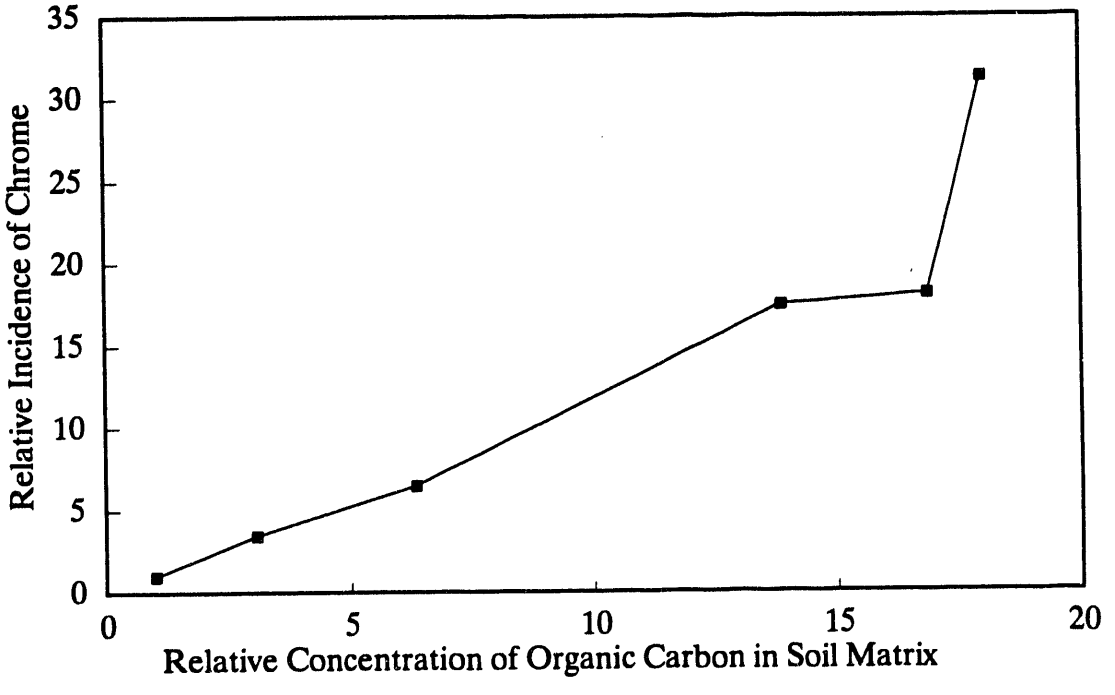



Figure 5.13 Correlation Test of Contamination vs. Soil Constituent, Chromium Distribution vs. Organic Carbon in Matrix.

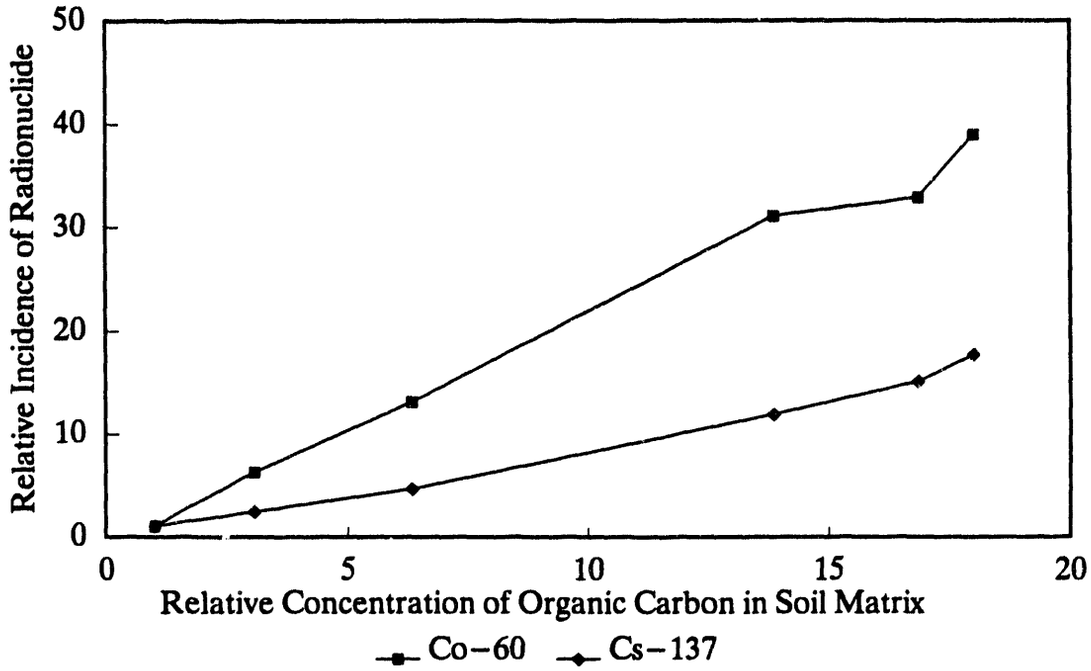



Figure 5.14 Correlation Test of Contamination vs. Soil Constituent, Radionuclide Distribution vs. Organic Carbon in Matrix.

The trends become more obvious on the plots of relative incidence of contaminants versus iron, manganese, and organic carbon. The curves for cesium are similar to those for cobalt which indicates the dominant fixation mechanisms for the cations may not be selective between the cations for the matrix elements analyzed, attracting them both in a similar manner. The chemical differences between the ions may be manifested only in the degree to which they are concentrated (slope of curve). For chromium, the correlation with manganese appears the most pronounced, however, this is not necessarily a cause and effect relationship, and the two species may just be coincident.

Interestingly, Figures 5.15 and 5.16 indicate possible inverse relationships to the silicon concentration. Other than a single low silicon value, the curves show a continuous decrease in contamination with increasing silicon content. This may indicate that the quartz grains are relatively inert to contaminant adsorption, and simply dilute the matrix,

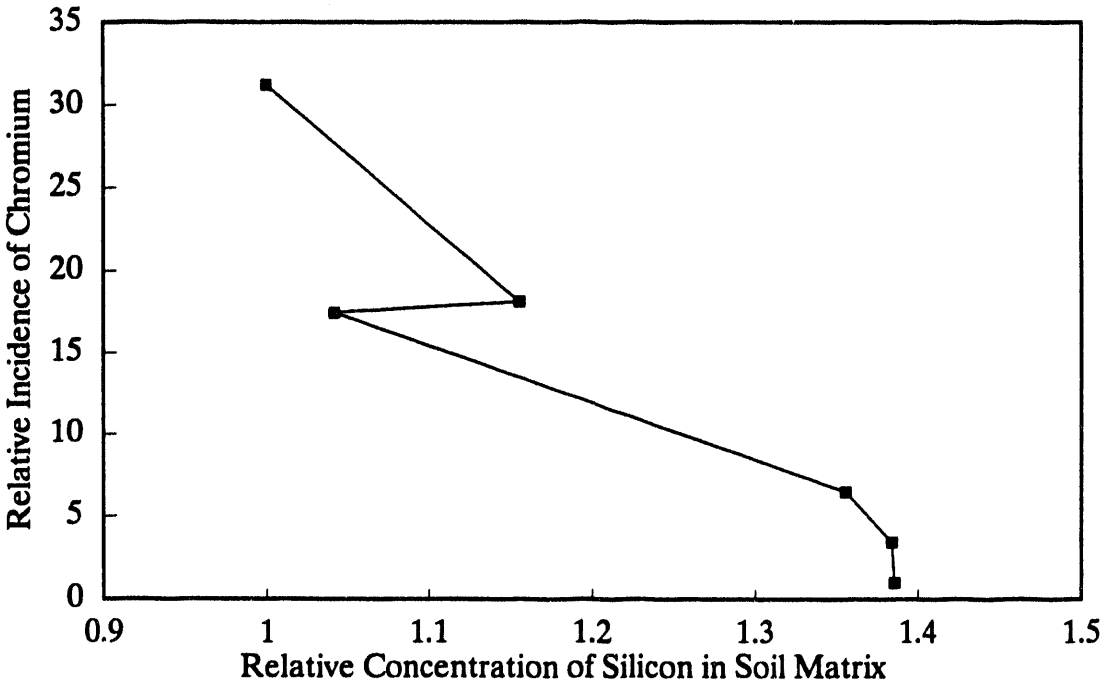



Figure 5.15 Correlation Test of Contamination vs. Soil Constituent, Chromium Distribution vs. Silicon in Matrix.

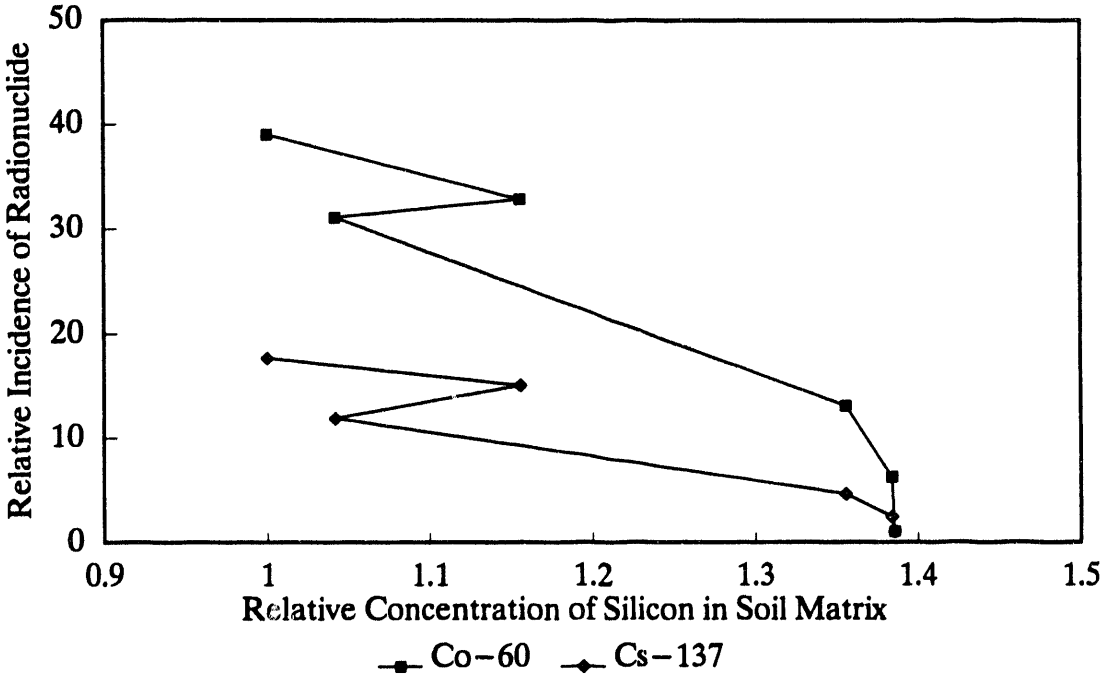



Figure 5.16 Correlation Test of Contamination vs. Soil Constituent, Radionuclide Distribution vs. Silicon in Matrix.

decreasing the adsorption capacity on a weight basis. Cesium sorption may be a function of the degree of silicon lattice substitution (silicate) rather than the amount of silicon (quartz) present.

D. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to provide both insight into the geometric nature of the particles, and elemental maps of the as-received particle surface. By mapping the surface of the particles for matrix constituents and contaminants, correlations may be observed that are not necessarily obvious from gross assays of total elemental makeup of the soil matrix. The SEM photographs shown in Figures 5.17 and 5.18 show the surface topography of two particles in the -40+100 mesh fraction. As can be seen at this relatively low magnification, the particles appear to be just minute versions of common river rock with rounded surfaces, and a few pits, but little or no porosity. Further examination of this particle size both topographically at very high magnification, and by elemental mapping for chromium provided no more insight. No porosity was apparent, and no areas of concentrated chromium contamination could be found.

Electron dispersive spectroscopy (EDS) was then used to generate the elemental spectrums shown in Figures 5.19, 5.20, and 5.21. Elements covering at least 0.1 percent of the scanned surface are shown in the spectrum. The gold (Au) peaks are caused by the surface coating applied during sample preparation to create a conductive surface, and the copper peaks (and possibly some of the zinc) are from the brass stud on which the sample is mounted. Note that significant peaks are shown for aluminum (Al), silicon (Si), sulfur (S), potassium (K), calcium (Ca), barium (Ba), chromium (Cr), iron (Fe), copper (Cu) and zinc (Zn), but cesium and cobalt are not indicated. This is due to the fact that the radionuclides occur at sub-parts-per-billion levels, and the limiting SEM sensitivity is six orders-of-magnitude greater. The radionuclides would have to be greatly concentrated at specific sites to be apparent.

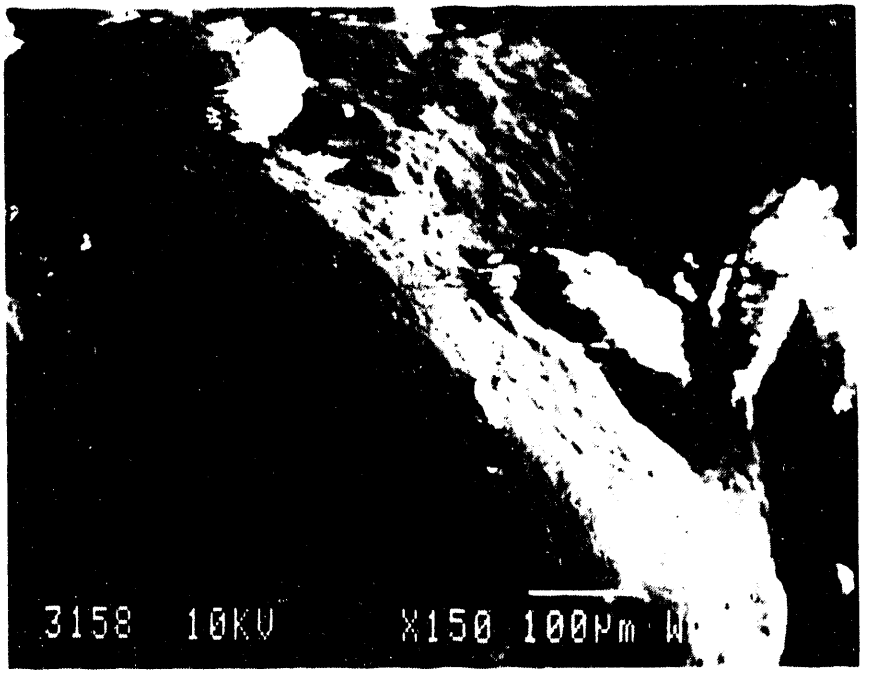



Figure 5.17 Surface Topography I, -40+100 Mesh.

Figure 5.18 Surface Topography II, -40+100 Mesh.

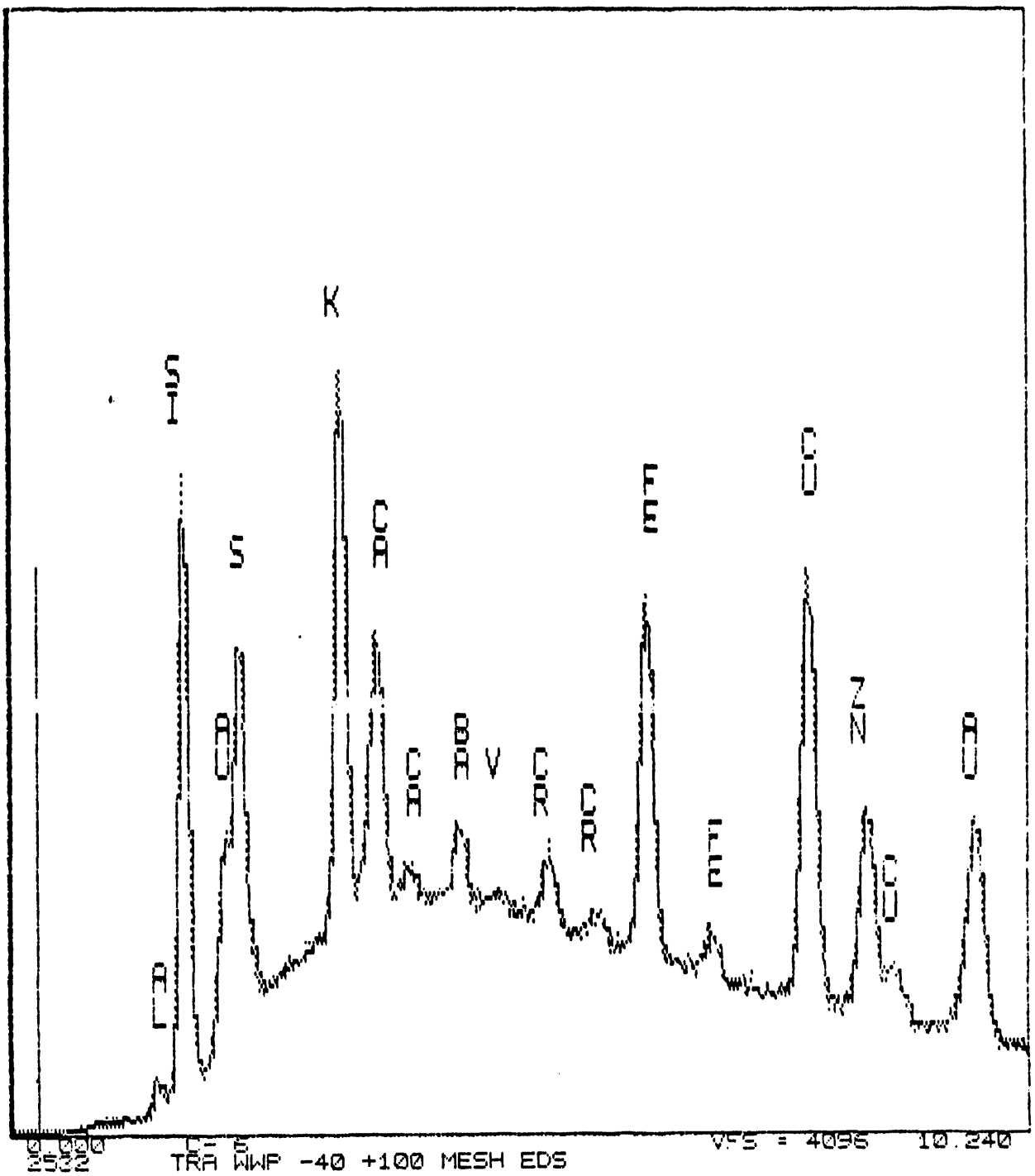



Figure 5.19 Electron Dispersive Spectrum of -40+100 Mesh Fraction.

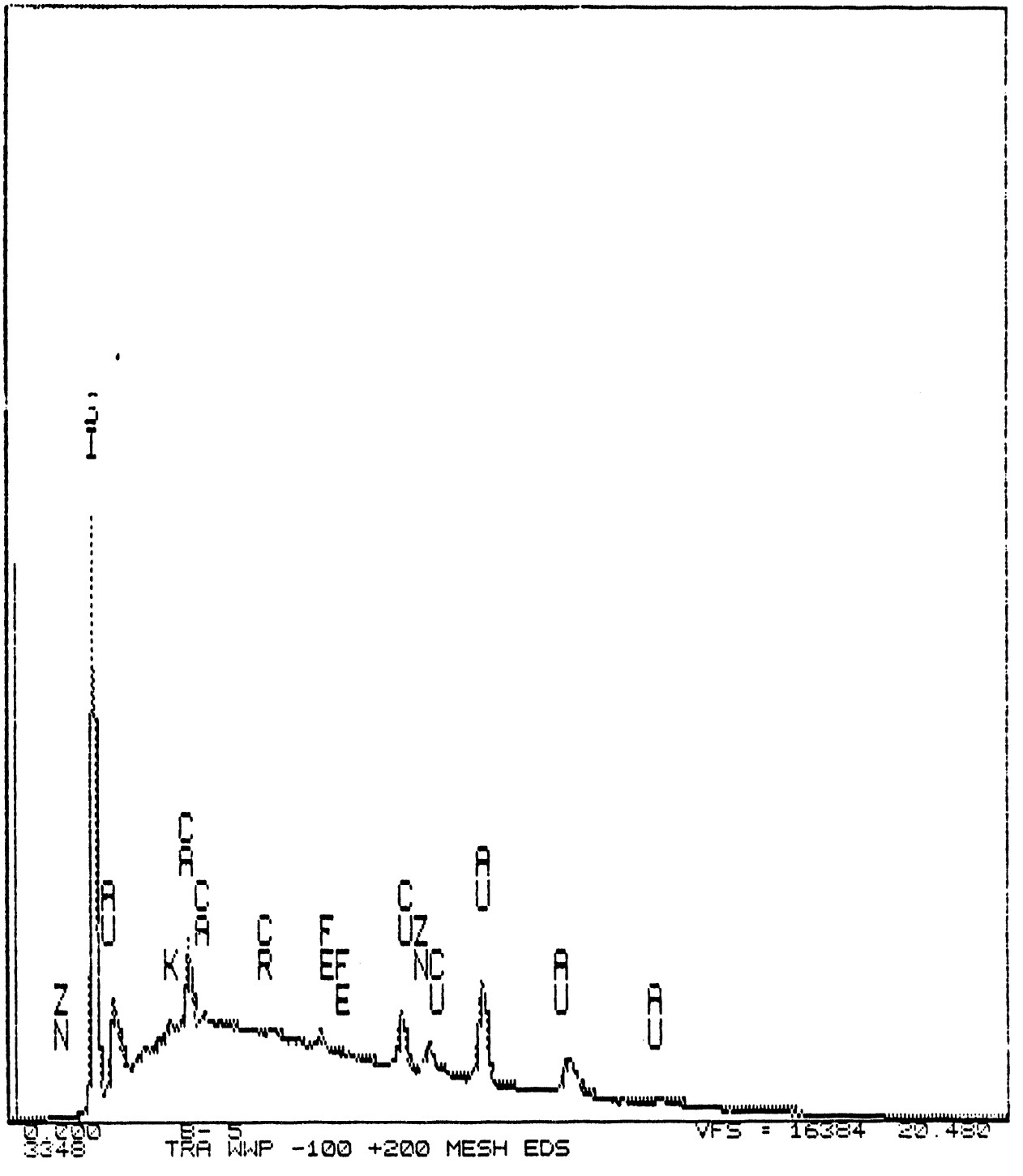



Figure 5.20 Electron Dispersive Spectrum of -100+200 Mesh Particle

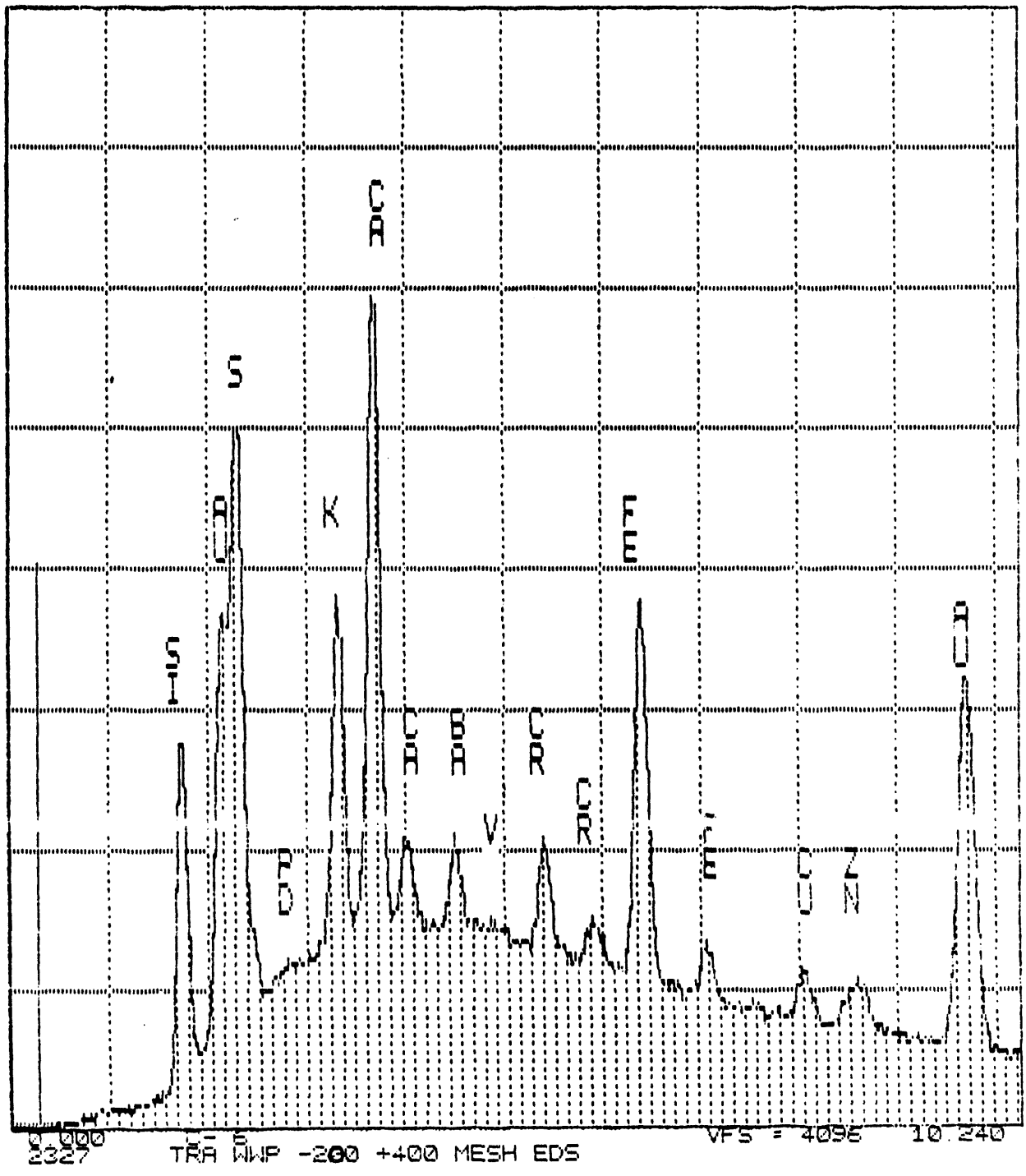



Figure 5.21 Electron Dispersive Spectrum of -200+400 Mesh Fraction.

Figures 5.22 through 5.24 display an area designated Site 1 of the mounted -200+400 mesh particle size. The first photo shows the actual surface at 100 times magnification, generated by backscatter electron imaging (BEI) of particles fixed in epoxy. The second photo shows slightly more detail using electrons of higher energy to penetrate the surface a few angstroms ($10^{-10}$m) producing a secondary electron image (SEI). As can be seen, the particles are mainly broken mineral fragments, not all as rounded as in the larger particle size, and some showing irregular precipitated deposits. The third photograph indicates the relative incidence of elements of higher mass, but very few sites stand out from the field.

Figure 5.25 is a dot map of the relative incidence of chromium in the same field covered by the surface topographs. Chromium is concentrated in the bright spots in the upper left corner. Comparing to Figures 5.26 and 5.27, dot maps of iron, and silicon respectively, it can be observed there is no correlation in this field between chromium and iron or silicon. It can be observed, however, that silicon is ubiquitous in the sample as expected, and the wide-spread incidence of iron suggests that an iron oxide film covers many of the particles.

Figures 5.28 through 5.33 and 5.34 through 5.40 are of two different groups of the -200+400 mesh particle size. This time the elemental mapping sequence shows a positive correlation of chromium with the incidence of iron which suggests the chromium may be fixed with oxides of iron on particle surfaces. Calcium and manganese are also coincident, but to a lesser extent. Silicon and carbon show no positive correlation. The last series of photomicrographs, (Figures 5.41-5.48) are for a single particle in the -100+200 mesh size. The dot maps show a slightly elevated level of chromium above background, with coincident concentrations of iron and manganese. Calcium is barely elevated, but the incidence of silicon stands out strongly against the high carbon epoxy potting compound. This is probably a flat cleavage plane of a silicate mineral covered with hydrated oxides of iron and manganese. The dot maps do not yield definitive proof of correlation of chromium with any one specific phase, but do indicate

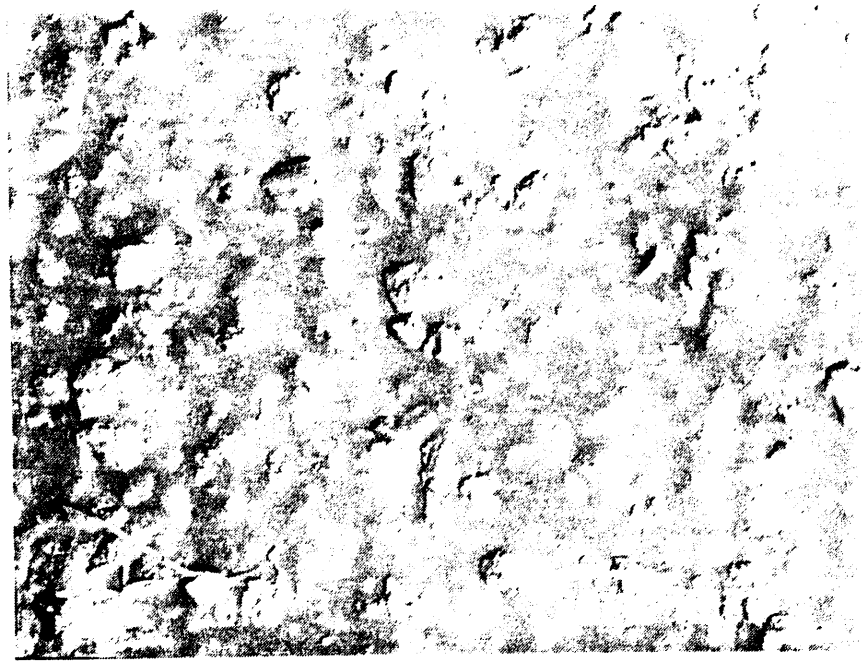


Figure 5.22 Surface Topography by Backscatter Electron Imaging (BEI), -200+400 Mesh, Site 1

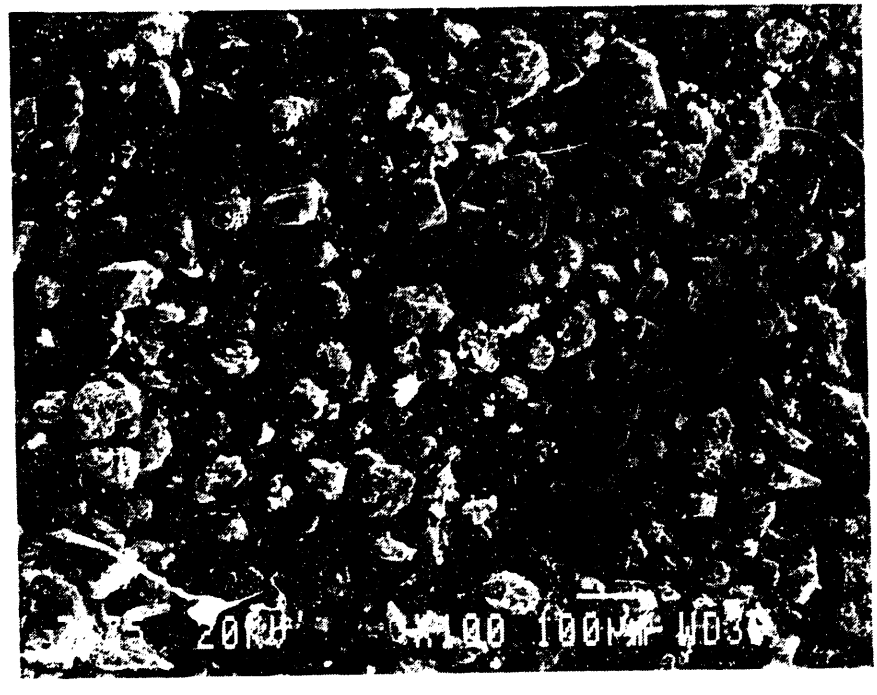


Figure 5.23 Surface Topography by Secondary Electron Imaging (SEI), -200+400 Mesh, Site 1

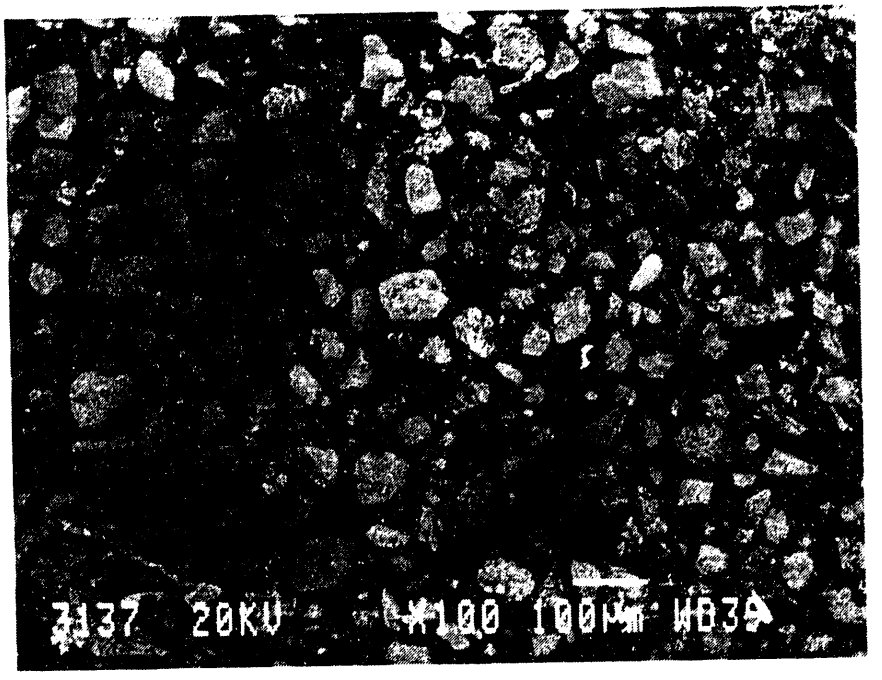



Figure 5.24 Compositional Scan, -200+400 Mesh, Site 1.

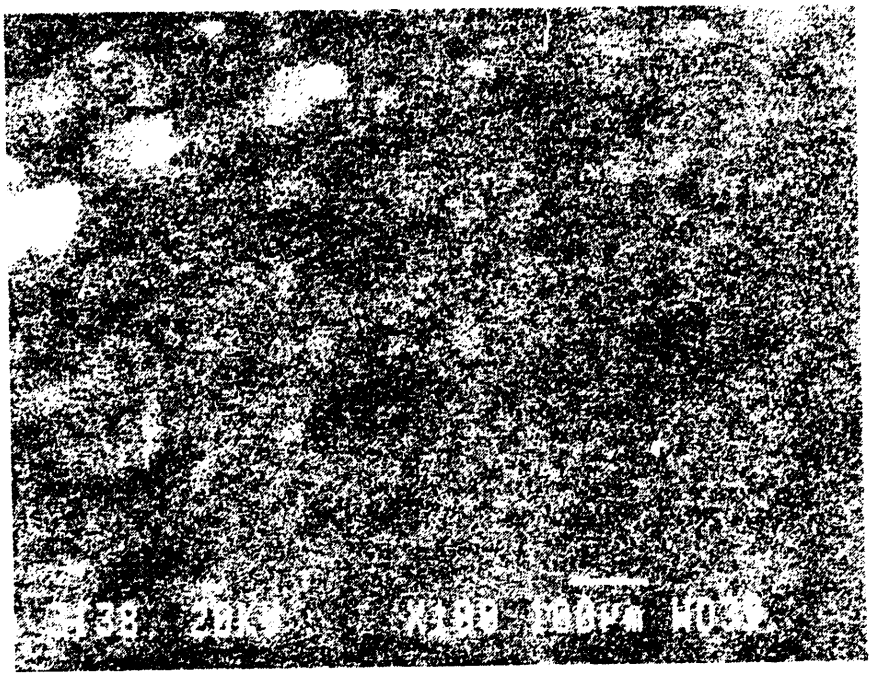


Figure 5.25 Chromium Dot Map, -200+400 Mesh, Site 1.

Figure 5.26 Iron Dot Map, -200+400 Mesh, Site 1.

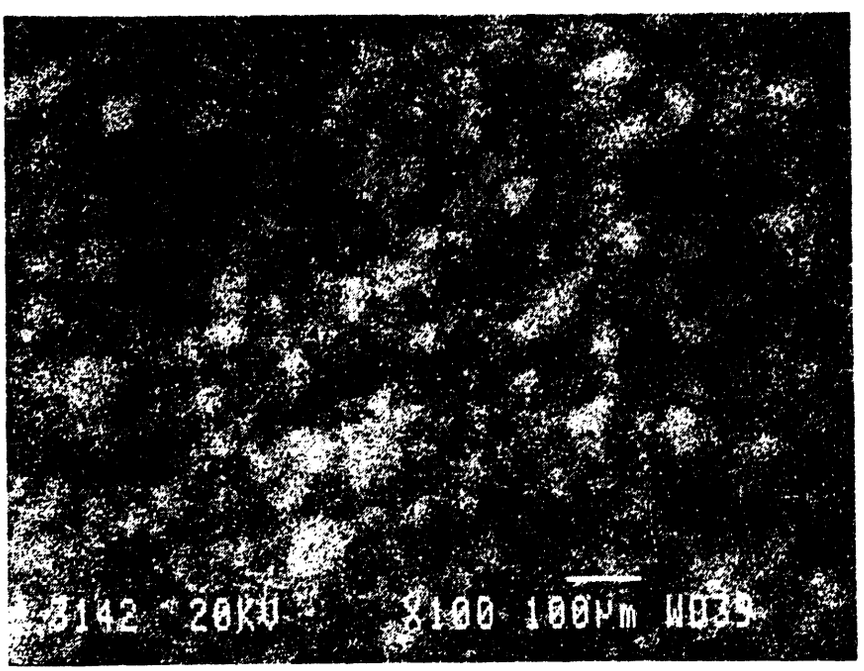



Figure 5.27 Silicon Dot Map, -200+400 Mesh, Site 1.

Figure 5.28 Surface Topography by Backscatter Electron Imaging (BEI), -200+400 Mesh, Site 2

Figure 5.29 Surface Topography by Secondary Electron Imaging (SEI), -200+400 Mesh, Site 2.

Figure 5.30 Compositional Scan, -200+400 Mesh, Site 2.

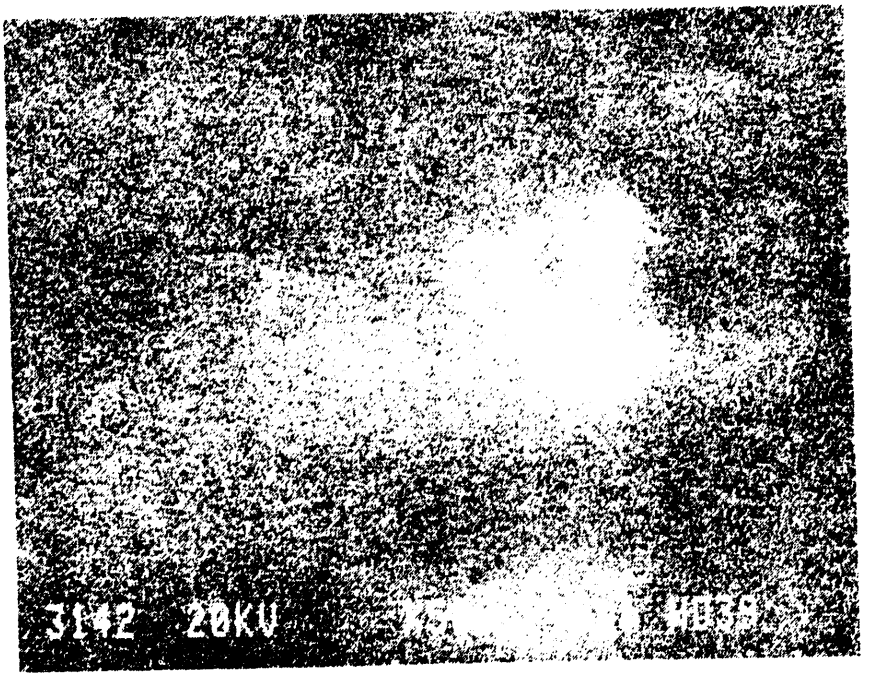



Figure 5.31 Chromium Dot Map, -200+400 Mesh, Site 2.

Figure 5.32 Iron Dot Map, -200+400 Mesh, Site 2.

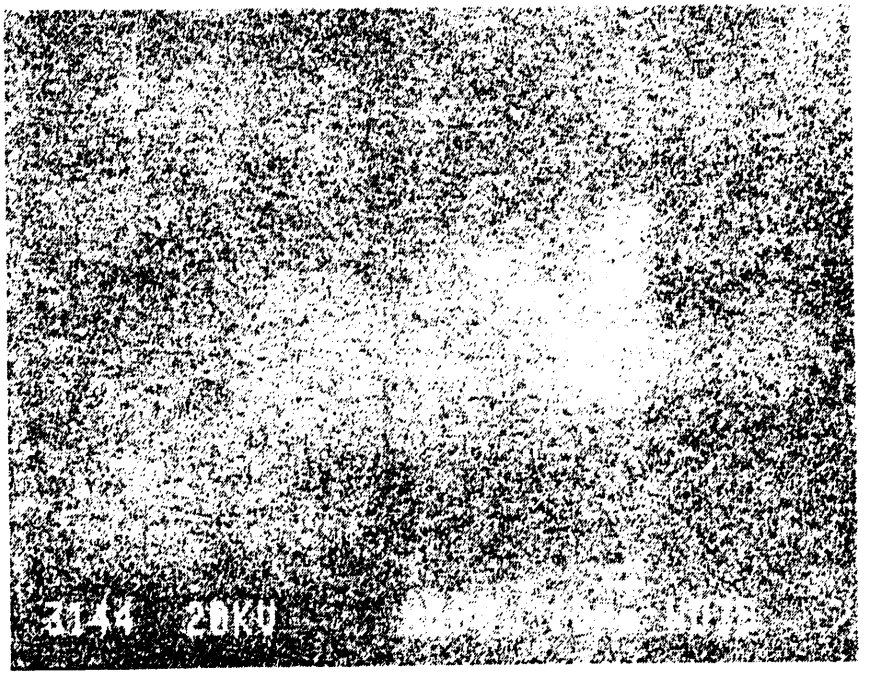


Figure 5.33 Manganese Dot Map, -200+400 Mesh, Site 2.

Figure 5.34 Surface Topography by Secondary Electron Imaging (SEI), -200+400 Mesh, Site 3

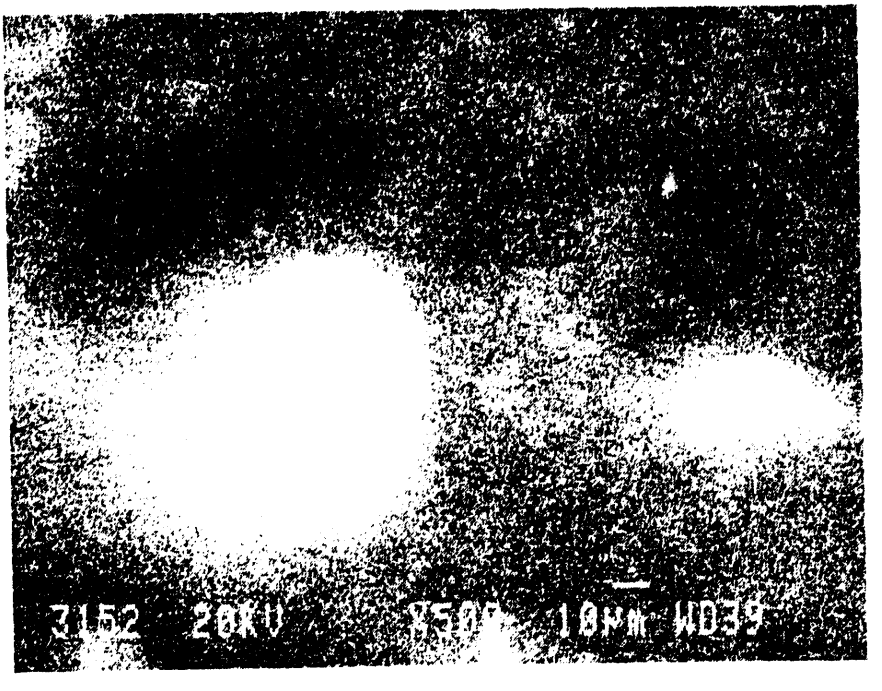


Figure 5.35 Chromium Dot Map, -200+400 Mesh, Site 3.

Figure 5.36 Iron Dot Map, -200+400 Mesh, Site 3.

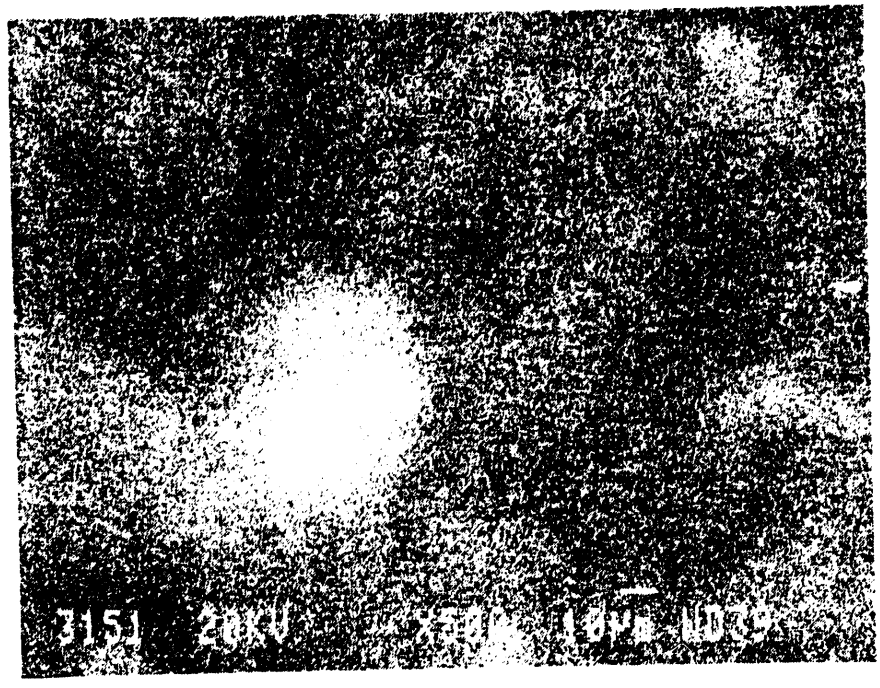


Figure 5.37 Manganese Dot Map, -200+400 Mesh, Site 3.

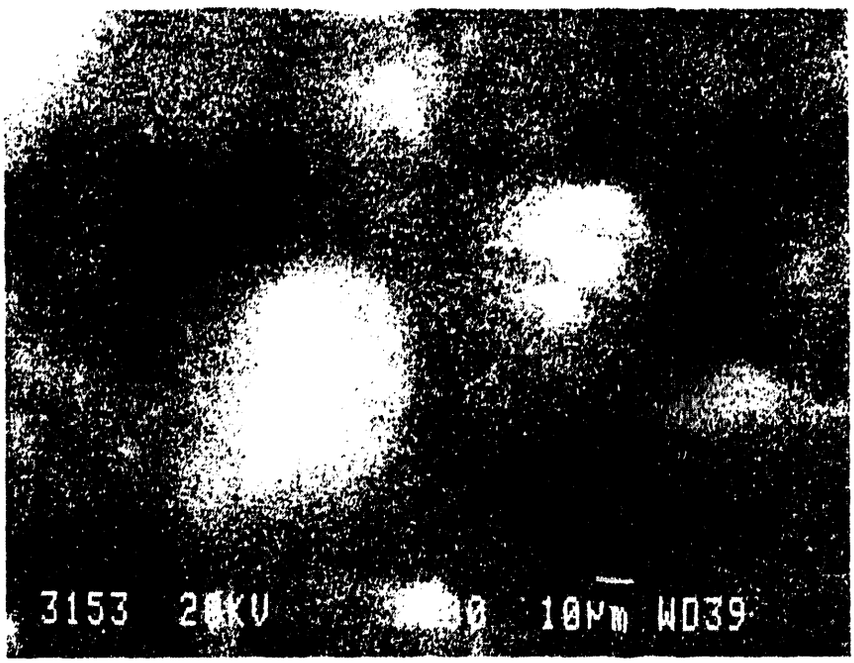



Figure 5.38 Calcium Dot Map, -200+400 Mesh, Site 3.

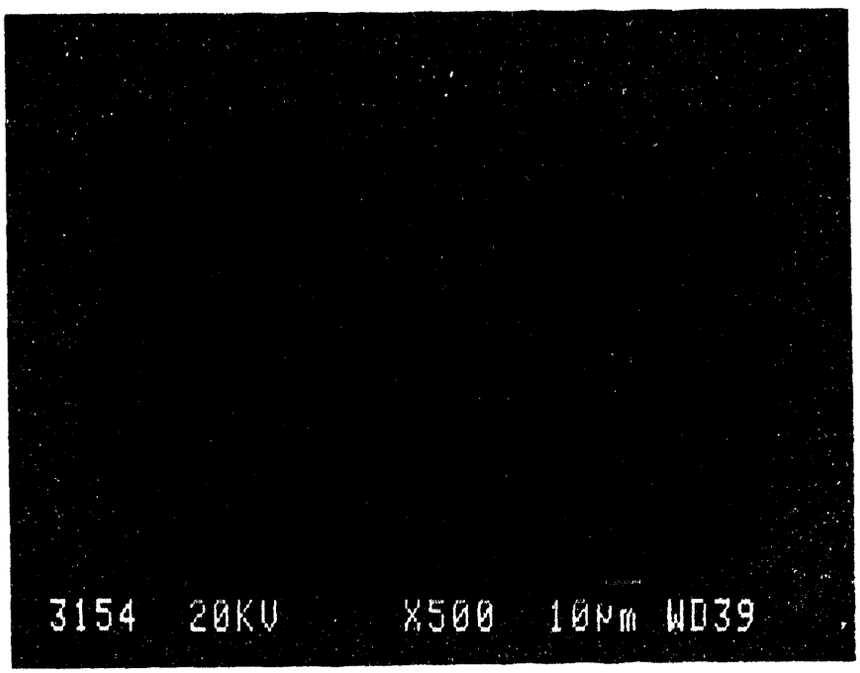



Figure 5.39 Silicon Dot Map, -200+400 Mesh, Site 3.

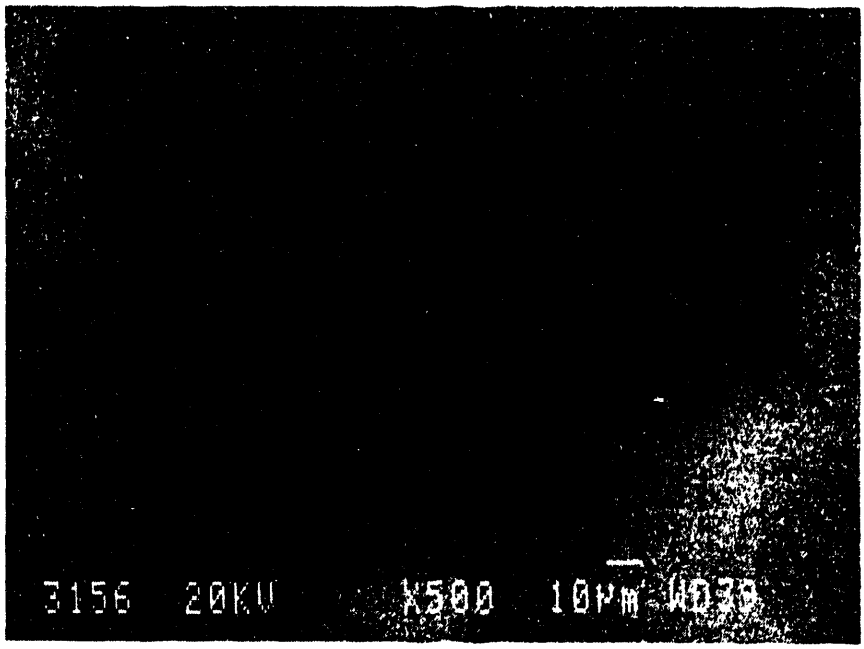



Figure 5.40 Carbon Dot Map, -200+400 Mesh, Site 3.

Figure 5.41 Compositional Scan, -100+200 Mesh Single Particle.

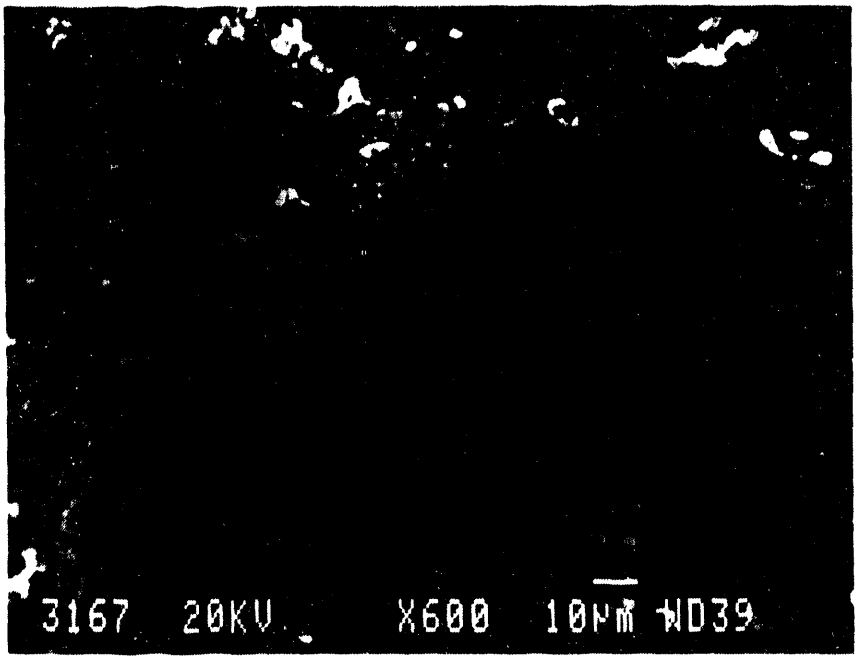



Figure 5.42 Same Particle, Higher Magnification of Upper Left

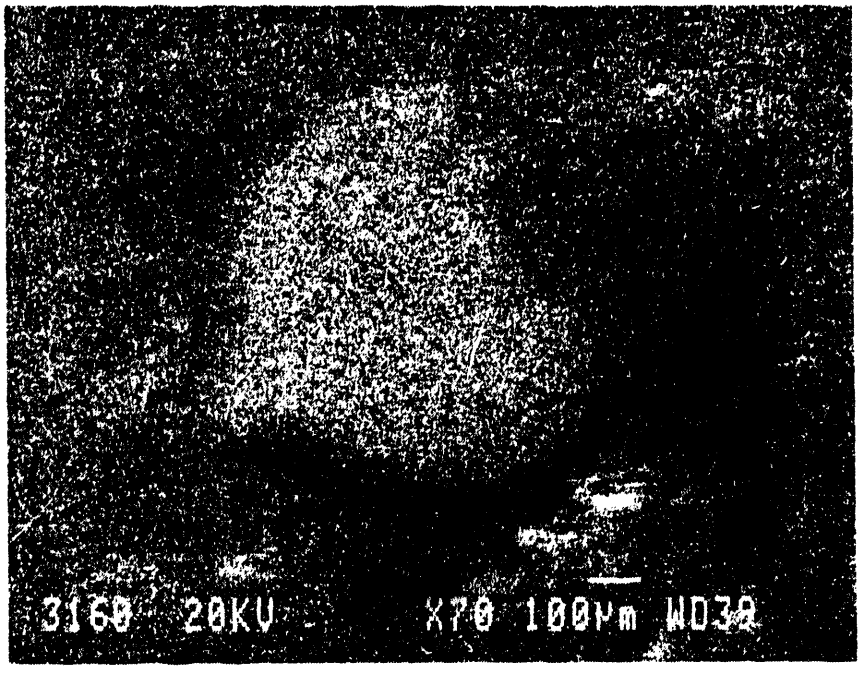



Figure 5.43 Chromium Dot Map, -100+200 Mesh Particle.

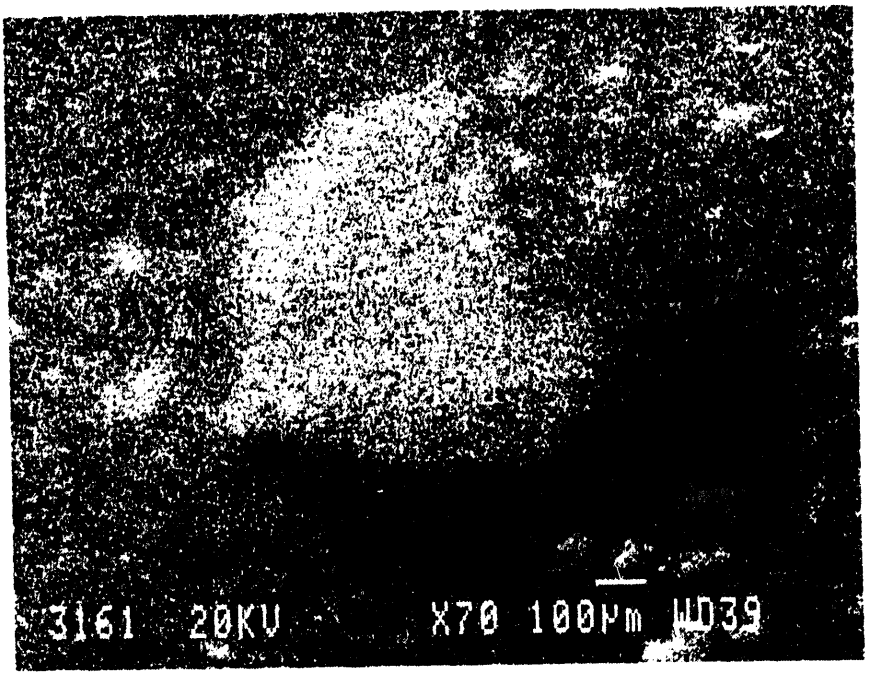



Figure 5.44 Iron Dot Map, -100+200 Mesh Particle.

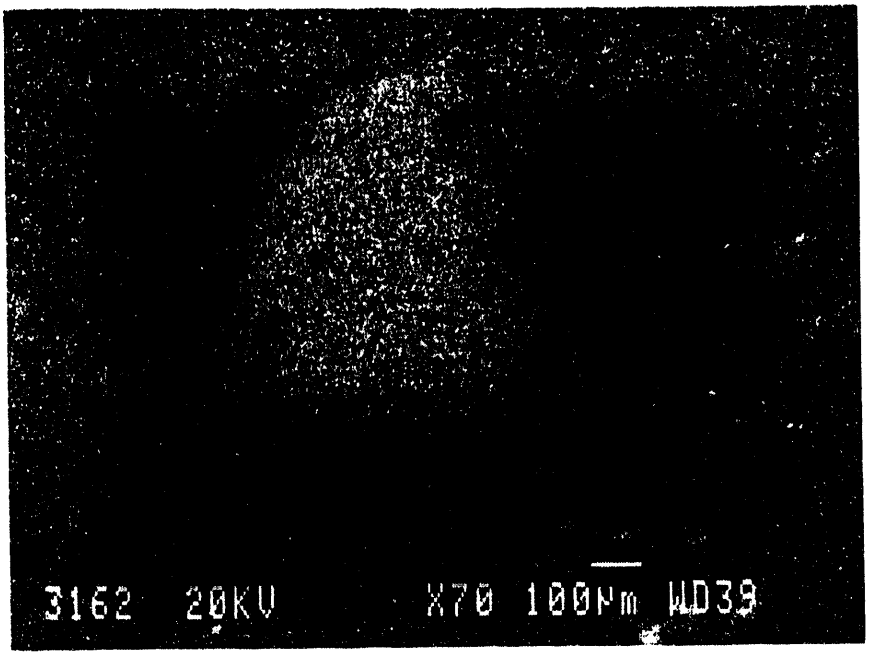



Figure 5.45 Manganese Dot Map, -100+200 Mesh Particle.

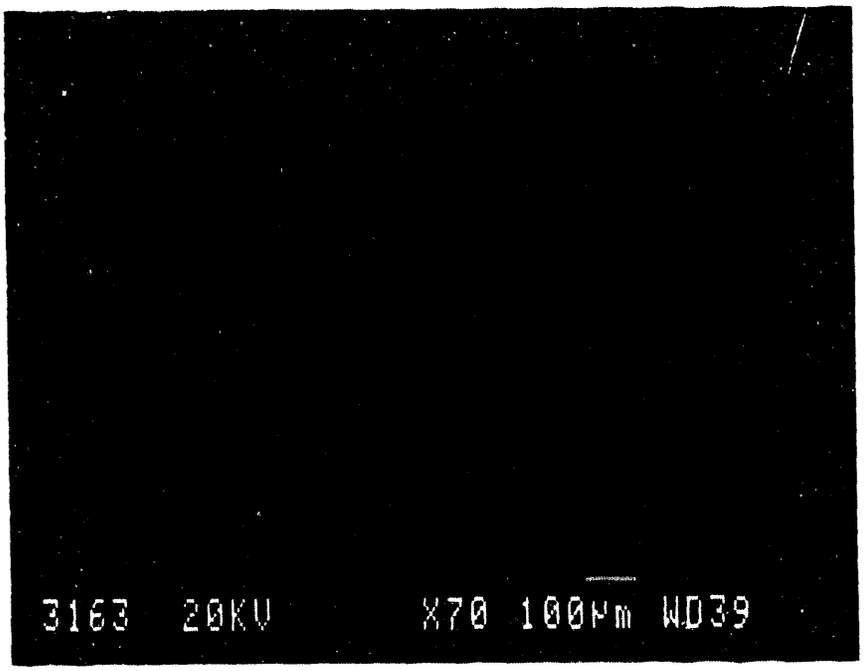



Figure 5.46 Calcium Dot Map, -100+200 Mesh Particle.

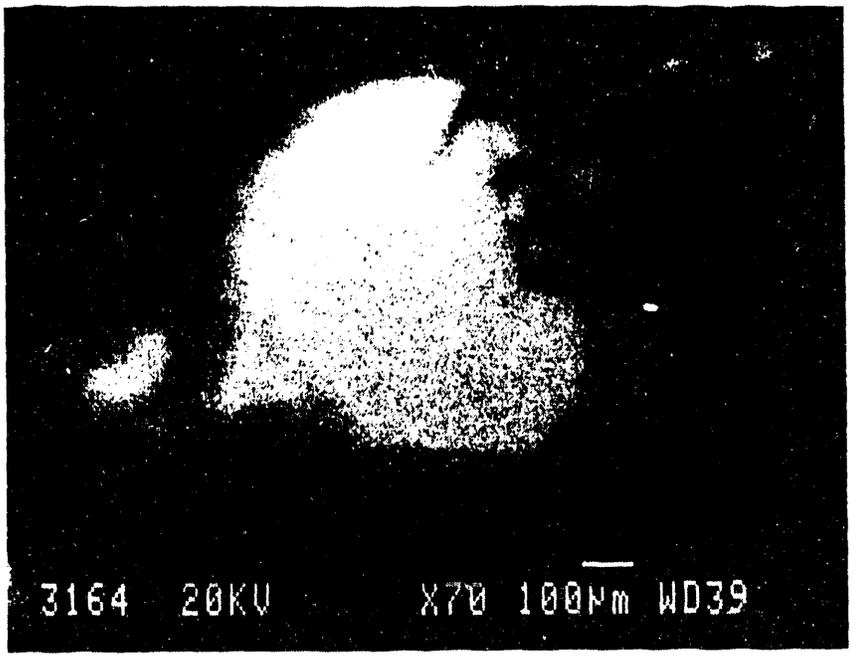


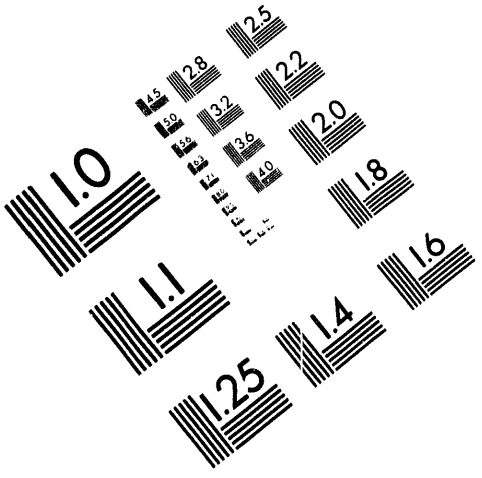

Figure 5.47 Silicon Dot Map, -100+400 Mesh Particle.

Figure 5.48 Carbon Dot Map, -100+200 Mesh Particle.

concentration of chromium in the surface deposits. Higher incidence of chromium is apparent only with weathering products which are dissolved in the sequential extractions.

E. X-ray Diffraction

Analysis by x-ray diffraction gives an indication of the probable major crystalline phases in the sample. The computer match of the diffraction peaks is not an exact determination, rather it provides a list of the most probable crystal structures present, and the relative amounts of each phase. Amorphous materials are not only indeterminate, but their magnitude relative to the crystalline phases cannot be accurately estimated. For these reasons, the data may not be simply compared to the elemental distribution. Of greater importance are the confirmation or denial of the existence of a suspect phase, and the trends indicated by the analyses. The relative incidence of five functionally grouped species most commonly



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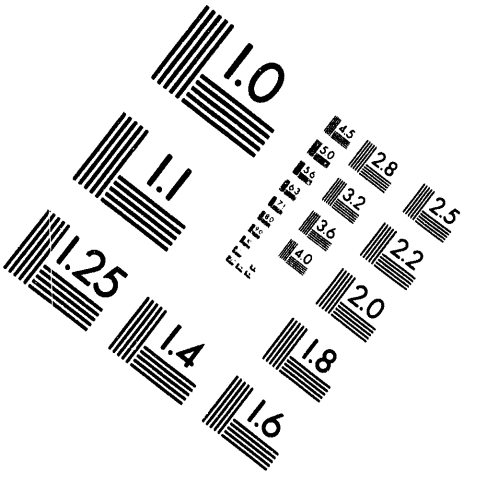
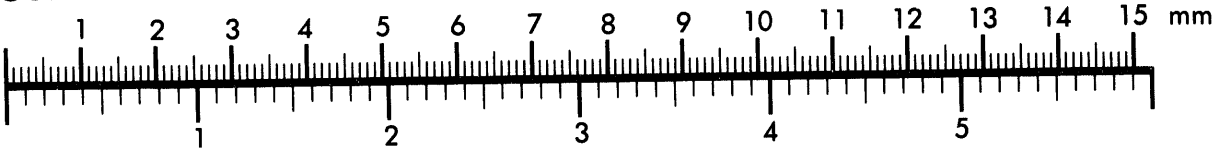
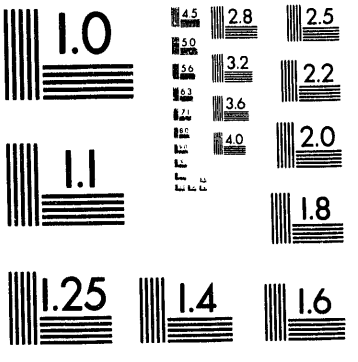
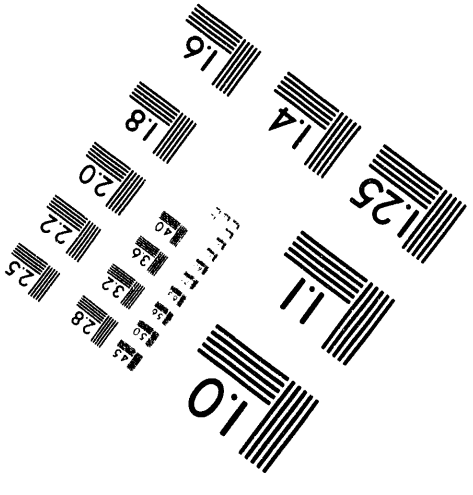


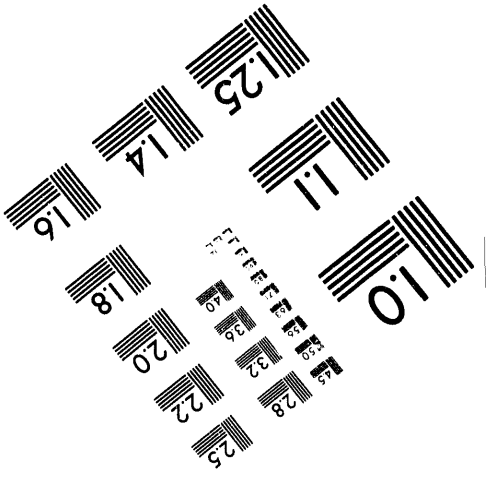
Centimeter



Inches







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2 of 2

found in the sample is summarized by particle size in Figure 5.49, and Table 5.4. In general, silica ($\alpha$-quartz) is the dominant crystalline phase in all but the finest sieve fraction, decreasing in magnitude with particle size. This is probably due to weathering of parent minerals and biological activity which accumulates metal oxides and organic detritus in the smaller particle sizes. Of notable exception is the -200+400 fraction which is as high in silica as the -4+10 fraction. This size range may include quartz particles that weather more slowly than larger conglomerates of mixed mineral. Feldspar grains (aluminosilicates substituted with mono- and di-valent cations) and mineral weathering products such as oxides of manganese and iron, and carbonates are present in all size fractions, with a greater prevalence in the smaller size fractions. Organic carbon cannot be detected by x-ray diffraction.

The diffraction data had no apparent correlation with the incidence of contaminants, either when tested as individual crystalline species, or when grouped functionally. The data do, however, confirm the presence of all crystalline species to be targeted by the sequential extractions, and provide some insight into the relative magnitudes of each phase. A complete listing of the relative abundance of crystalline phases by particle size is provided in Appendix B.

F. Representative Sample

Combining the characterization data by weight fraction, a representative sample composited from the -40 mesh material has the calculated characteristics summarized in Table 5.5. These numbers are only about 10% lower than measured values for an actual composited sample, which verifies the compositing accuracy.

Radionuclide activity per gram is sufficient for calculating some risk scenarios, but provides no insight for most readers into the relative amounts of each element present in the soil. To evaluate the extraction data, the values in Table 5.5 must be converted using half life values

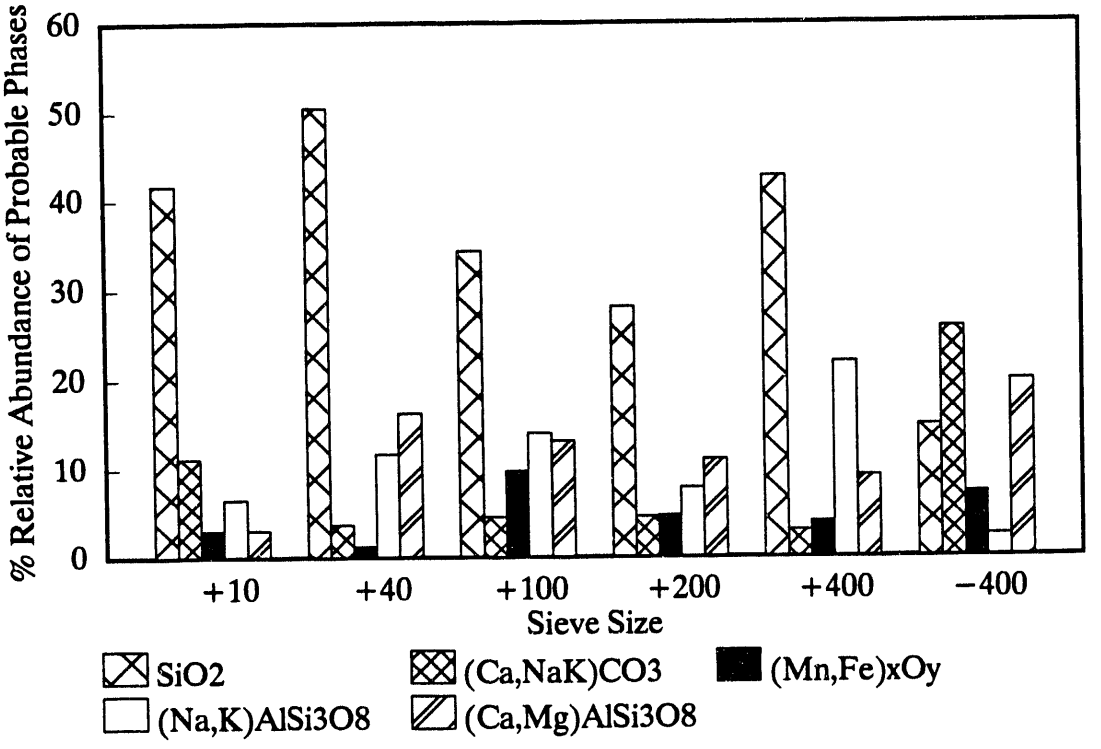


Figure 5.49 X-ray Diffraction Data by Particle Size Functionally Grouped Major Crystalline Phases.

Table 5.4 Functionally Grouped Crystalline Phases Distribution by Particle Size

| Sieve Size | $SiO_2$ | $(Ca,NaK)CO_3$ | $(Fe,Mn)_xO_y$ | $(Na,K)AlSi_3O_8$ | $CaAl_2Si_2O_8$ |
|---|---|---|---|---|---|
| +4 | <---------- No Representative Sample ----------> | | | | |
| +10 | 41.7 | 11.1 | 3 | 6.5 | 3.0 |
| +40 | 50.5 | 3.6 | 1.2 | 11.6 | 16.2 |
| +100 | 34.3 | 4.5 | 9.7 | 13.9 | 13.1 |
| +200 | 28.1 | 4.5 | 4.6 | 7.8 | 11.0 |
| +400 | 42.7 | 2.9 | 3.9 | 21.9 | 9.1 |
| -400 | 14.8 | 25.7 | 7.2 | 2.3 | 19.8 |

| Table 5.5 Representative -40 Mesh Sample Description | | | |
|---|---|---|---|
| Characteristic | Average | Element | wt% |
| Particle Diameter ($\mu m$) | 171 | Silicon | 26.93 |
| Particle Density ($g/cm^3$) | 2.59 | Aluminum | 4.63 |
| Cesium Activity (pCi/g) | 41445 | Calcium | 2.05 |
| Cobalt Activity (pCi/g) | 9327 | Organic C | 2.66 |
| Total $\gamma$-Activity (pCi/g) | 50772 | Iron | 2.27 |
| Chromium Contamination (ppm) | 3135 | Manganese | 0.11 |

($Cs^{137}$: $t^{1/2}$=30.17yr, $Co^{60}$: $t^{1/2}$=5.271yr), and atomic weights ($Cs^{137}$: AW=136.9068g, $Co^{60}$: AW=59.9338g). Hence, the cesium concentration in the sample is 0.48ppb, and the cobalt concentration is 8.24ppt. Soil washing to remove contaminants at these concentrations has never been accomplished.

## III. SEQUENTIAL EXTRACTIONS

### A. Time-Release Profiles

The duration of each extraction step outlined in the original plan was selected or estimated based on the available literature to ensure complete dissolution of the target matrix component.[3,4,5,6] In conflict with this goal is the potential for contaminants to resorb to different types of sites on the solid residue during the extraction. This would produce a cascade of contaminant species from one type of site to another as the dominant fixation sites are destroyed by dissolution.

To test this hypothesis, time release studies of net contaminant release were done with and without a potassium nitrate brine to inhibit the resorption of the cesium. Extraction solutions were analyzed after varying exposure times to determine optimum conditions for cesium release in the

carbonate and easily and moderately reducible phase dissolutions. Cesium was tracked for the optimization because it is the dominant risk driver in the site risk analysis, and its strong $\gamma$-emission signature allows very sensitive monitoring of incremental changes over time. Potassium was chosen as the displacing ion because it is closest in size, charge, and chemistry to cesium, and therefore has the greatest potential for penetrating and displacing cesium from adsorption sites as described in Chapter 4.

The first mechanistic assumption necessary for analyzing the applicability of the model presented in Chapter 3 is that the matrix element chosen to monitor the progress of the dissolution is relatively unaffected by resorption (i.e., the extractant is effective not only in dissolving a phase, but in keeping it in solution). The profiles for calcium during the carbonate extraction, manganese for the easily-reducible metal-oxide extraction, and iron for the moderately-reducible metal-oxide extraction are shown in Figure 5.50. Initial calcium release appears to be accelerated by the brine, but the time-to-plateau and steady-state concentrations appear constant with and without the counter-ion present. The curves with and without the brine are essentially congruent for the other two matrix elements. Thus the extractant is effective and any brine effects observed in the contaminant profiles probably result from resorption.

The brine effects on the carbonate extraction are illustrated by the profiles in Figure 5.51. Radionuclide concentration is plotted as disintegrations per second per milliliter of solution (dps/ml) versus time. Net release of cobalt is increased by a factor of about two, cesium by about five-fold by addition of brine. The required extraction duration to ensure complete carbonate extraction was less well defined. The profile shown in Figure 5.51 shows a prompt release followed by a gradual increase in calcium (micrograms per milliliter (ug/ml) and radionuclides over 1080 minutes (18 hours), with no definite plateau indicating the completion of the carbonate dissolution. A longer term study to define the entire

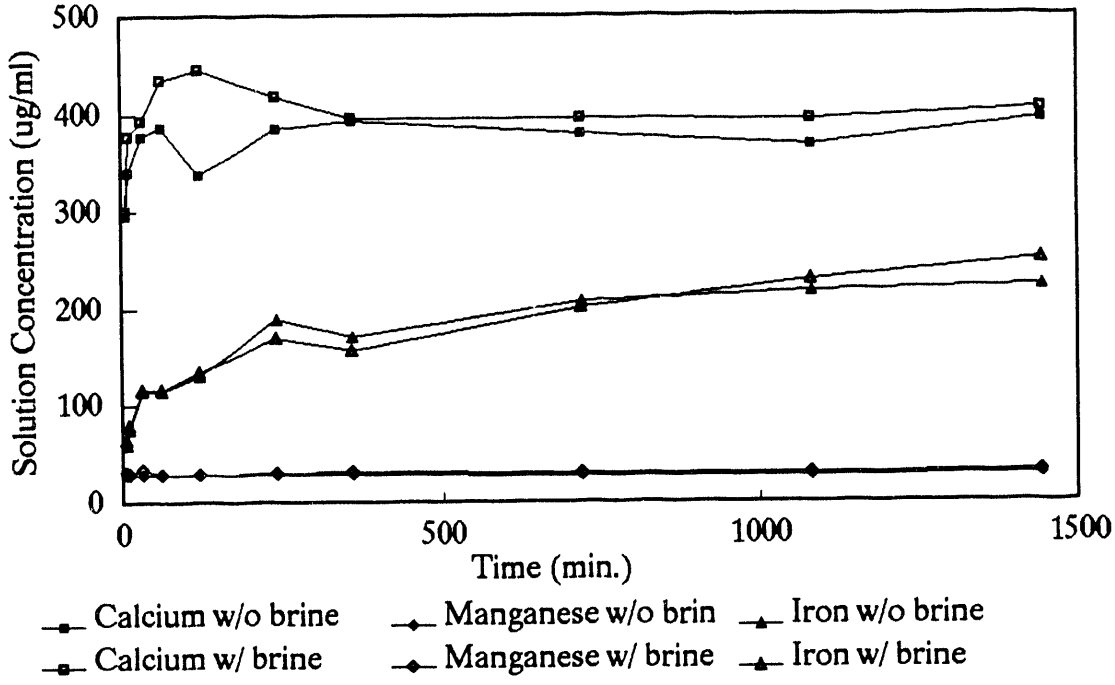


Figure 5.50 Matrix Element Time Release Profile, with and without $KNO_3$ Brine to Control Resorption

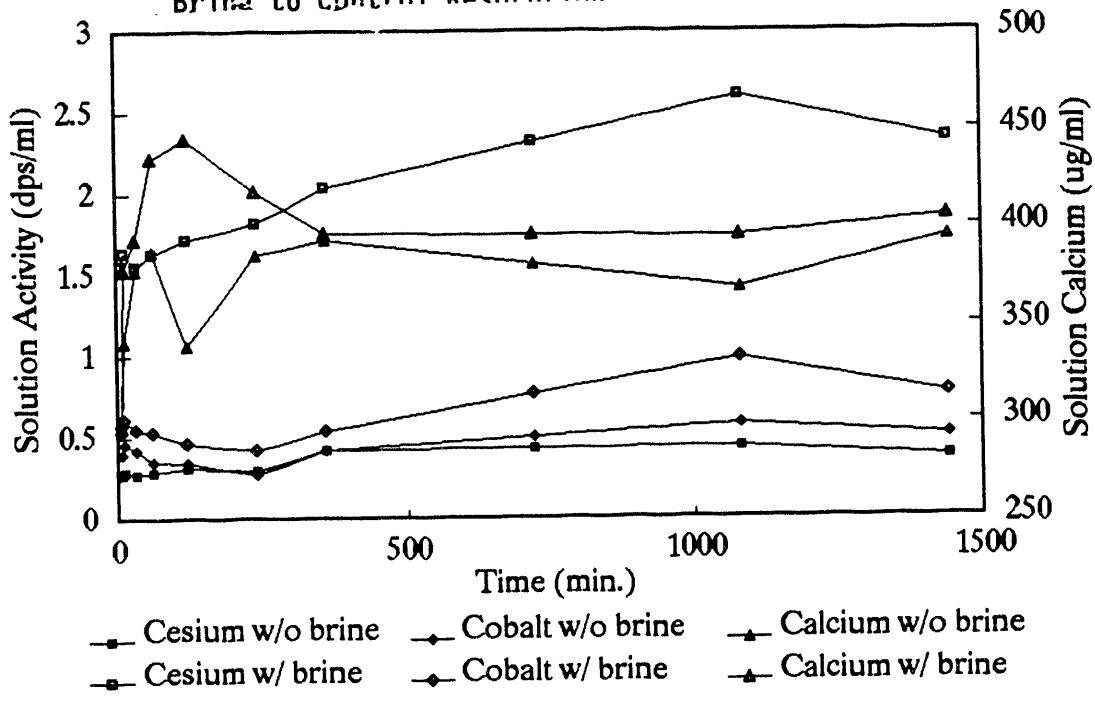


Figure 5.51 Radionuclide Release Profile for Carbonate Extraction With (w/) and Without (w/o) KNO3 Brine to Control Resorption

profile was then run for 48 hours. While there was still no obvious endpoint, the radionuclide levels did not increase appreciably beyond about 24 hours. In addition, inorganic carbon analyses of the residue and extract indicated about 80% destruction of the carbonate, but increasing non-selective attack on the manganese and iron phases. (Non-selective extraction of the metal-oxides was not entirely prevented by control of the pH as indicated by a gradually increasing wine color in the extraction solutions, and later verified by analysis.) Thus, while it is conceivable additional decontamination could be accomplished using the carbonate extractant, the extraction time selected was 24 hours as a compromise between extraction efficiency and selectivity. Any residual carbonate was destroyed in later extractions.

Net release of the metals chromium, manganese and iron during the carbonate extraction continues almost linearly through four hours, with a gradual decrease in rate for an additional 14 hours (Figure 5.52). The counter-ion accelerates the apparent initial rate of metal extraction by 90-100%, but after about 18 hours the net release is only increased by 30-40%. The gradual continuous release of additional activity tracks roughly with the continuous release of metals, which may reflect some of the nonspecific dissolution beyond the targeted carbonate phase.

This data suggests significant resorption occurs naturally on the same time-scale as the dissolution, such that sites are filled as soon as they are available. Without the brine present, the decontamination available by dissolving the carbonate phase would be grossly underestimated for cesium. The potassium brine appears to be more specific than predicted, with a much lesser impact on the metals relative to the effect on cesium. Similarity in hydrated ionic size and charge are probably controlling factors.

Although iron and calcium continue to be released for at least 24 hours (Figures 5.53 and 5.54), the easily-reducible phase extraction as monitored by the manganese release is essentially complete in the first several minutes of exposure (Figure 5.53). The continued release may be due to

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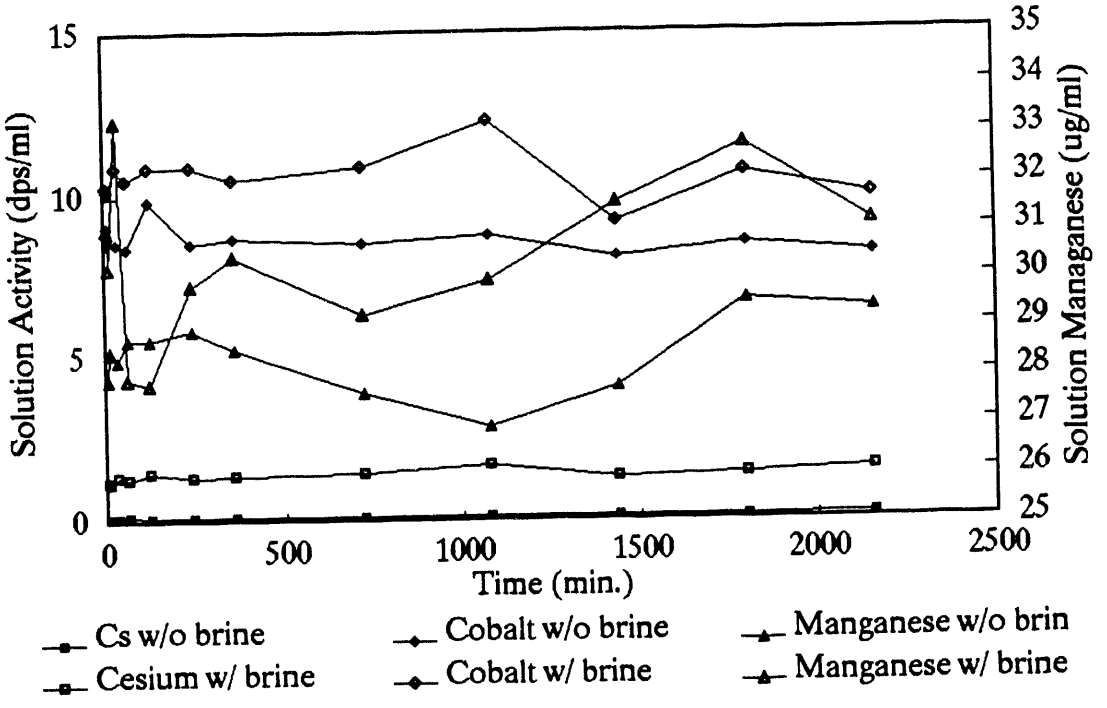


Figure 5.54 Radionuclide Time Release Profile for Easily-Reducible Phase Extraction With (w/) and Without (w/o) KNO3 Brine to Control Resorption

slow attack on partially amorphous iron-oxides, and the extractant destroying residual carbonates (calcium) not dissolved earlier. The figures also show the release of the contaminants, chromium, cesium and cobalt is essentially complete in less than an hour. To ensure complete destruction of the carbonate phase, the extraction duration was increased to 18 hours.

The counter-ion appears to increase the calcium and cobalt release by about 20%, but the cesium release is increased by over an order of magnitude. Interestingly, after a peak at about 30 minutes, the solution chromium concentration continues to decrease for the duration of the extraction. The counter-ion appears to double the net release of chromium, but only slows the loss from solution. None of the other analyte concentrations show a consistent decline over the duration of the experiment. This decay in chromium concentration indicates a slower resorption of chromium

relative to the other analytes.

The extraction profiles for all monitored elements during the moderately-reducible metal-oxide extraction show a significant reduction in slope at about 30 minutes, and again at 4 hours (240 minutes), but a more gradual release continues for at least 48 hours. Figures 5.55 and 5.56 show the general trends in changing slope over a 36 hour period. Solution manganese and calcium show a continuous increase, but are two orders of magnitude lower than the iron release. This confirms the prior extractions were effective, as any residual calcium carbonate or manganese oxide would also be dissolved in this step. The gains in net extraction due to the counter-ion are 30% for calcium, 20% for chromium, and 10% for cesium. Manganese and cobalt show no gain due to the counter-ion, which may simply reflect a lack of these metals available after the earlier extractions. There is no indication of slow resorption for any of the analytes. To maximize destruction of the phase, the extraction duration was increased 50% over the time-study period, to 72 hours.

In general, the experiments indicated very rapid resorption of the cesium and cobalt. None of the curves for the radionuclides have a negative slope indicating a gradual loss from the solutions as shown for chromium in Figure 5.53. In all cases enhancement of extraction due to addition of the brine is manifested by an upward shift in the entire release profile. The magnitude of the brine effect was substantially greater for cesium than cobalt. This apparent selectivity may be attributed to two equally plausible causes: 1) potassium may, in fact, specifically displace cesium over cobalt, or 2) cesium may simply have a greater tendency for resorption, so its net release is affected more by any counter ion. Neither of these possibilities may be ruled out entirely by the data. However, some insight may be gained from the easily-reducible phase extraction results. Assuming no synergistic effect on dissolution by the brine, the difference in release between the experiments with and without brine is the amount that resorbs. Noting that the brine produces a ten-fold increase in cesium release in the easily-reducible phase extraction

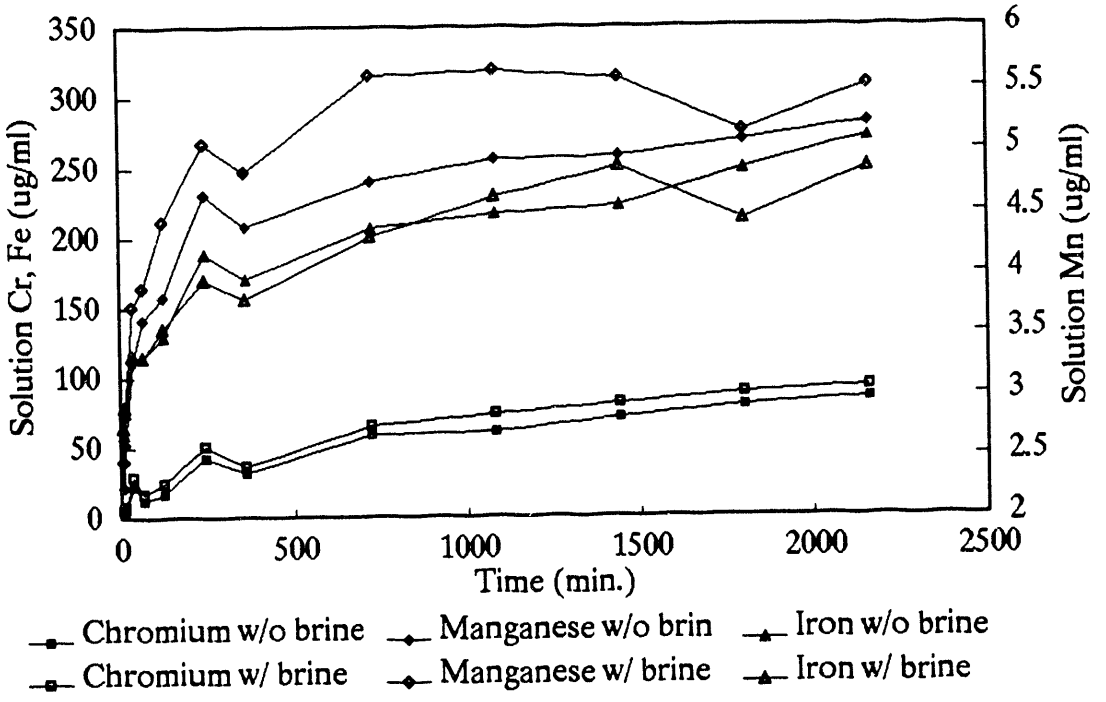


Figure 5.55 Metals Time Release Profile for Moderately-Reducible Phase Extraction With (w/) and Without w/KNO3 Brine to Control Resorption

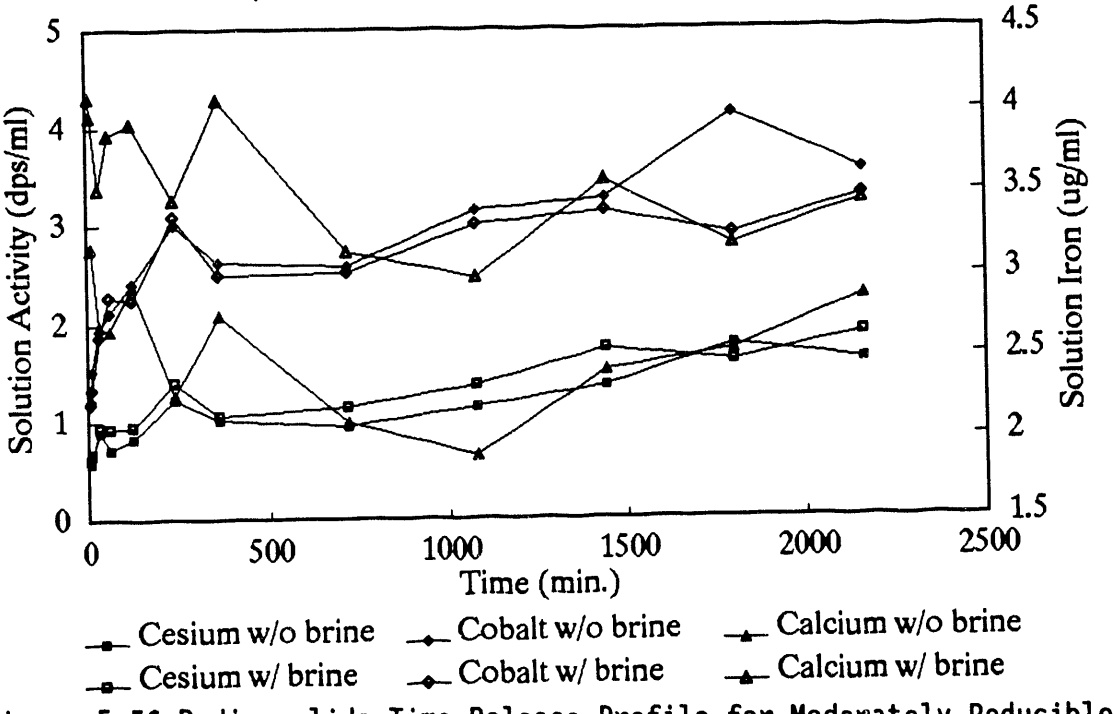


Figure 5.56 Radionuclide Time Release Profile for Moderately-Reducible Phase Extraction With (w/) and Without (w/o) KNO3 Brine to Control Resorption

(Figure 5.54), it can be concluded that about 90% of the cesium can resorb under these conditions and only 10% of the extracted cesium stays in solution without the brine present. This relationship does not hold for cobalt under the same conditions. The net release of cobalt without brine is 50-60% of the total available in the sample. Clearly less than 90% of the released cobalt resorbs. At parts-per-trillion levels, it is extremely unlikely that the adsorption capacity of the residual solid is limiting, therefore the tendency for cobalt resorption on the remaining sites must be less than that for cesium regardless of the selectivity of the brine. Thus, though the magnitude of the brine effect is probably primarily a function of the Hofmeister series, it is also at least partially an indication of the contaminants affinity for resorption on the remaining solid.

B. Mass Dissolution

Air-dried samples were weighed before and after each extraction to estimate the mass dissolved in each step. Repeatedly transferring the material back and forth from centrifuge tubes used for extraction, solids separation, and rinsing to petri dishes used to expedite drying proved too cumbersome to provide reliable data. In addition, two samples were lost in the organic digestion step, when the concentrated peroxide extractant reacted violently with the high surface area samples containing about 2.5 wt% organic material. The remaining two samples indicated a cumulative weight loss of about 22 and 26 wt% over the five extractions (Table 5.6). Observation suggests each determination might be 0.5 to 1.0 wt% high, for a nominal weight loss of as much as 20 wt%. Figure 5.57 illustrates the relative mass dissolution for each extraction.

Samples 1-4 were carried through the entire sequential extraction, versus samples 5-8 which were new samples for each extraction. A comparison of the data on a weight basis alone indicates comparable dissolution whether the sample was previously exposed or not, with the exception of the easily reducible extraction which dissolves about 50% more material from a virgin

Table 5.6 TRA Warm Waste Pond - Sequential Extraction Weight Loss
All data in grams

| Sample No. | Initial Weight | Ion-X Final Weight | Ion-X % loss | CO3 Final Weight | CO3 % loss | MnOx Final Weight | MnOx % loss | FeOx Final Weight | FeOx % loss | Organic Final Weight | Organic % loss | Total % loss |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.9703 | 1.9154 | 2.8 | 1.7869 | 6.5 | 1.7211 | 3.3 | 1.6124 | 5.5 | 1.4671 | 7.4 | 25.54 |
| 2 | 1.9881 | 1.9611 | 1.4 | 1.8610 | 5.0 | 1.7938 | 3.4 | 1.7210 | 3.7 | lost | lost | lost |
| 3 | 1.9681 | 1.9067 | 3.1 | 1.8106 | 4.9 | 1.7281 | 4.2 | 1.6530 | 3.8 | lost | lost | lost |
| 4 | 2.0093 | 1.9750 | 1.7 | 1.9272 | 2.4 | 1.7989 | 6.4 | 1.7102 | 4.4 | 1.5707 | 6.9 | 21.83 |
| Ave | 1.9840 | 1.9396 | 2.2 | 1.8464 | 4.7 | 1.7605 | 4.3 | 1.6742 | 4.4 | 0.7595 | 3.6 | 23.68 |
| 5 | 1.9365 | 1.9005 | 1.9 | | 5.2 | | 9.0 | | 1.9 | | 3.0 | 21.03 |
| 6 | 2.0766 | 2.0346 | 2.0 | | 4.7 | | 6.2 | | 4.4 | | 4.0 | 21.28 |
| 7 | 2.0000 | Ave Val-> | 1.9 | | 3.9 | | 6.9 | | 3.8 | | 4.0 | 20.64 |
| 8 | 2.0504 | Ave Val-> | 2.0 | | 4.7 | | 4.4 | | 3.7 | | 3.9 | 18.67 |
| Ave | 2.0159 | 1.9676 | 2.0 | | 4.6 | | 6.6 | | 3.4 | | 3.7 | 20.40 |
| 9 | 1.9607 | <- Values used for estimating | | | | | | | | | | |
| 10 | 2.0408 | initial contamination or | | | | | | | | | | |
| 11 | 1.9972 | matrix element content only. | | | | | | | | | | |
| 12 | 2.0454 | | | | | | | | | | | |

Analyst felt 0.5 to 1.0% overstated in each step due to losses in transfer

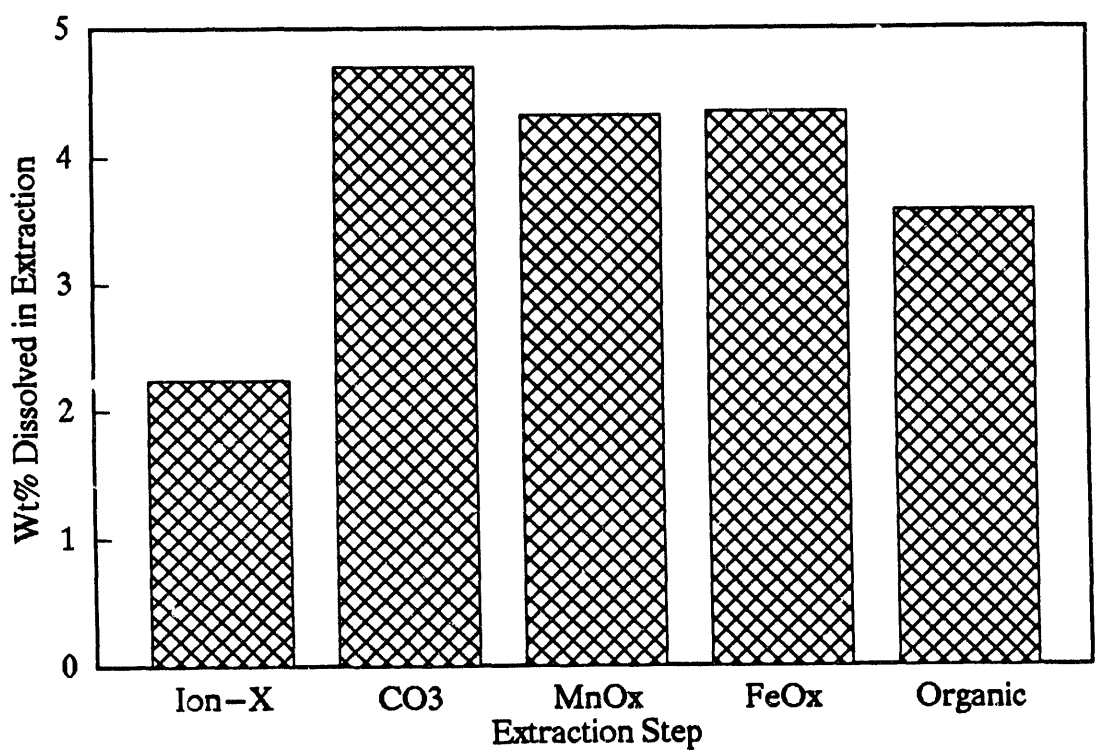


Figure 5.57 Weight % Dissolved by Extraction

sample. Comparison on an elemental basis indicates that weight loss alone is not adequate to evaluate the selectivity of the extractions. In most cases, the virgin samples do indeed yield more contamination than the previously extracted samples, indicating some non-specific attack as the extractants become more corrosive.

## C. Release Data

### 1. Tabular Data

Radionuclide release in the extractions was essentially the same as that predicted by the time studies, confirming the reproducibility of data using this technique. Tables 5.7 and 5.8 show the total activity released in each extraction, and the percentage of the total that release represents based on the initial weight of the samples, and the average measured activity in a composited sample. Samples 1-4 were used for the initial ion-exchange step, then carried forward to generate weight loss data only. The average release by ion-exchange from these four samples was used to calculate closure for samples 5-12. The data from samples 9-12 provide the basis for calculating the contaminant distribution. The last two columns contain: 1) a summation of the total amount extracted plus that found in the final residue, and 2) a percent closure based on the total accounted for versus the amount estimated in the original sample based on weight. Tables 5.9 through 5.17, for chromium and soil matrix constituents are organized in the same manner.

### 2. Radionuclide Release

Total cesium and cobalt release was 18% and 84%, respectively. Triplicate sample extraction variability for cesium ranged from 1 to 31%, with 82-86% for cobalt. Summing the released activity with that measured in the final residue dissolution, a closure of about 86% and 104% for cesium and cobalt respectively was obtained. This

## Table 5.7 TRA Warm Waste Pond - Sequential Extraction Cesium Decontamination, All data in disintegrations per second (dps)

| Sample No. | Initial Cesium | Ion-X Cesium Released | % decon | CO3 Cesium Released | % decon | MnOx Cesium Released | % decon | FeOx Cesium Released | % decon | Organic Cesium Released | % decon | Lattice Cesium Released | % left | Cesium Released | Activity Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3302 | 260 | 7.9 | | | | | | | | | | | | |
| 2 | 3332 | 218 | 6.6 | | | | | | | | | | | | |
| 3 | 3299 | 242 | 7.3 | | | | | | | | | | | | |
| Ave | 3311 | 240 | 7.3 | | | | | | | | | | | | |
| 5 | 3391 | | | 263 | 7.7 | 271 | 8.0 | 494 | 14.6 | 321 | 9.5 | 2307 | 68.0 | 3901 | 115.0 |
| 6 | 3463 | | | 244 | 7.0 | 286 | 8.3 | 470 | 13.6 | 338 | 9.8 | 2645 | 76.4 | 4234 | 122.3 |
| 7 | 3352 | | | 259 | 7.7 | 240 | 7.2 | 474 | 14.1 | 347 | 10.4 | 2380 | 71.0 | 3943 | 117.6 |
| 8 | 3436 | | | 248 | 7.2 | 255 | 7.4 | 502 | 14.6 | 339 | 9.9 | 2789 | 81.1 | 4382 | 127.5 |
| Ave | 3411 | | | 253 | 7.4 | 263 | 7.7 | 485 | 14.2 | 336 | 9.9 | 2530 | 74.1 | 4115 | 120.6 |
| 9 | 3286 | | | 66 | 2.1 | 36 | 1.1 | 73 | 2.2 | 112 | 3.4 | 2118 | 64.4 | 2645 | 80.5 |
| 10 | 3420 | | | 71 | 2.1 | 40 | 1.2 | 72 | 2.1 | 96 | 2.9 | 2040 | 59.6 | 2569 | 75.1 |
| 11 | 3347 | | | 69 | 2.1 | 37 | 1.1 | 86 | 2.6 | 92 | 2.8 | 2437 | 72.8 | 2964 | 88.5 |
| 12 | 3428 | | | 65 | 1.9 | 34 | 1.0 | 75 | 2.2 | 130 | 3.8 | 2925 | 85.3 | 3478 | 101.5 |
| Ave | 3370 | | | 68 | 2.0 | 37 | 1.1 | 77 | 2.3 | 108 | 3.2 | 2360 | 70.5 | 2914 | 86.4 |
| Adjusted to 100% ------> | | | 8.4 | | 2.3 | | 1.3 | | 2.6 | | 3.7 | | 81.7 | | 100.0 |

## Table 5.8 TRA Warm Waste Pond - Sequential Extraction Cobalt Decontamination, All data in disintegrations per second (dps)

| Sample No. | Initial Cobalt | Ion-X Cobalt Released | % decon | CO3 Cobalt Released | % decon | MnOx Cobalt Released | % decon | FeOx Cobalt Released | % decon | Organic Cobalt Released | % decon | Lattice Cobalt Released | % left | Cobalt Released | Activity Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 666 | n/d | 0.0 | | | | | | | | | | | | |
| 2 | 672 | n/d | 0.0 | | | | | | | | | | | | |
| 3 | 665 | n/d | 0.0 | | | | | | | | | | | | |
| Ave | 668 | n/d | 0.0 | | | | | | | | | | | | |
| 5 | 684 | | | 32 | 4.6 | 474 | 69.3 | 229 | 33.4 | 6 | 0.9 | 603 | 88.2 | 1343 | 196.4 |
| 6 | 696 | | | 29 | 4.1 | 467 | 66.9 | 330 | 47.3 | 9 | 1.2 | 688 | 98.5 | 1523 | 218.0 |
| 7 | 676 | | | 28 | 4.2 | 433 | 64.0 | 236 | 34.9 | 8 | 1.2 | 674 | 99.7 | 1379 | 204.0 |
| 8 | 693 | | | 30 | 4.3 | 434 | 62.6 | 224 | 32.4 | 7 | 0.9 | 705 | 101.8 | 1400 | 202.0 |
| Ave | 688 | | | 29 | 4.3 | 452 | 65.7 | 255 | 37.0 | 7 | 1.1 | 668 | 97.0 | 1411 | 205.1 |
| 9 | 663 | | | 38 | 5.7 | 470 | 71.0 | 54 | 8.2 | 25 | 3.7 | 124 | 18.7 | 711 | 107.3 |
| 10 | 690 | | | 42 | 6.1 | 497 | 72.1 | 64 | 9.3 | 24 | 3.4 | 104 | 15.0 | 731 | 106.0 |
| 11 | 675 | | | 36 | 5.3 | 463 | 68.5 | 60 | 8.9 | 24 | 3.5 | 103 | 15.2 | 685 | 101.5 |
| 12 | 691 | | | 37 | 5.3 | 448 | 64.7 | 59 | 8.5 | 28 | 4.0 | 125 | 18.1 | 696 | 100.6 |
| Ave | 680 | | | 38 | 5.6 | 470 | 69.1 | 59 | 8.7 | 25 | 3.7 | 114 | 16.8 | 706 | 103.8 |
| Adjusted to 100% ------> | | | 0.0 | | 5.4 | | 66.5 | | 8.4 | | 3.5 | | 16.1 | | 100.0 |

## Table 5.9 TRA Warm Waste Pond - Sequential Extraction Chrome Decontamination, All data in grams

| Sample No. | Average Initial Chrome | Ion-X Chrome Released | % decon | CO3 Chrome Released | % decon | MnOx Chrome Released | % decon | FeOx Chrome Released | % decon | Organic Chrome Released | % decon | Lattice Chrome Released | % left | Chrome Released | Mass Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0067 | 5.94E-06 | 0.1 | | | | | | | | | | | | |
| 2 | 0.0068 | 5.94E-06 | 0.1 | | | | | | | | | | | | |
| 3 | 0.0067 | 5.94E-06 | 0.1 | | | | | | | | | | | | |
| Ave | 0.0067 | 5.94E-06 | 0.1 | | | | | | | | | | | | |
| 5 | 0.0069 | | | 6.90E-04 | 10.0 | 3.56E-04 | 5.2 | 5.97E-03 | 86.8 | 1.72E-03 | 24.9 | 6.41E-03 | 93.2 | 1.51E-02 | 220.3 |
| 6 | 0.0070 | | | 6.66E-04 | 9.5 | 2.09E-04 | 3.0 | 6.12E-03 | 87.1 | 2.02E-03 | 28.8 | 6.69E-03 | 95.3 | 1.57E-02 | 223.8 |
| 7 | 0.0068 | | | 6.42E-04 | 9.4 | 2.15E-04 | 3.2 | 6.48E-03 | 95.3 | 1.89E-03 | 27.8 | 6.49E-03 | 95.5 | 1.57E-02 | 231.3 |
| 8 | 0.0070 | | | 6.84E-04 | 9.8 | 2.47E-04 | 3.5 | 5.96E-03 | 85.5 | 2.08E-03 | 29.9 | 6.73E-03 | 96.6 | 1.57E-02 | 225.4 |
| Ave | 0.0069 | | | 6.71E-04 | 9.7 | 2.57E-04 | 3.7 | 6.13E-03 | 88.7 | 1.93E-03 | 27.8 | 6.58E-03 | 95.1 | 1.56E-02 | 225.2 |
| 9 | 0.0067 | | | 6.36E-04 | 9.5 | 5.28E-04 | 7.9 | 4.45E-03 | 66.7 | 1.76E-03 | 26.4 | 5.28E-04 | 7.9 | 7.90E-03 | 118.6 |
| 10 | 0.0069 | | | 6.60E-04 | 9.5 | 3.72E-04 | 5.4 | 4.69E-03 | 67.6 | 1.85E-03 | 26.6 | 5.40E-04 | 7.8 | 8.12E-03 | 117.0 |
| 11 | 0.0068 | | | 6.12E-04 | 9.0 | 4.78E-04 | 7.0 | 4.30E-03 | 63.4 | 1.80E-03 | 26.5 | 5.25E-04 | 7.7 | 7.72E-03 | 113.8 |
| 12 | 0.0070 | | | 6.12E-04 | 8.8 | 4.87E-04 | 7.0 | 4.31E-03 | 62.0 | 1.71E-03 | 24.6 | 5.70E-04 | 8.2 | 7.69E-03 | 110.7 |
| Ave | 0.0068 | | | 6.30E-04 | 9.2 | 4.66E-04 | 6.8 | 4.44E-03 | 64.9 | 1.78E-03 | 26.0 | 5.41E-04 | 7.9 | 7.86E-03 | 115.0 |
| Adjusted to 100% ------> | | | 0.1 | | 8.0 | | 5.9 | | 56.5 | | 22.6 | | 6.9 | | 100.0 |

## Table 5.10 TRA Warm Waste Pond - Sequential Extraction Calcium Dissolution, All data in grams

| Sample No. | Initial Calcium | Ion-X Calcium Released | % diss | CO3 Calcium Released | % diss | MnOx Calcium Released | % diss | FeOx Calcium Released | % diss | Organic Calcium Released | % diss | Lattice Calcium Released | % left | Calcium Released | Mass Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0433 | 5.71E-03 | 13.2 | | | | | | | | | | | | |
| 2 | 0.0437 | 5.56E-03 | 12.7 | | | | | | | | | | | | |
| 3 | 0.0433 | 5.72E-03 | 13.2 | | | | | | | | | | | | |
| Ave | 0.0435 | 5.67E-03 | 13.0 | | | | | | | | | | | | |
| 5 | 0.0445 | | | 2.48E-02 | 55.8 | 2.36E-02 | 53.1 | 1.56E-04 | 0.4 | 7.36E-03 | 17.2 | 4.65E-02 | 104.5 | 1.09E-01 | 244.0 |
| 6 | 0.0455 | | | 2.55E-02 | 56.1 | 2.53E-02 | 55.6 | 1.91E-04 | 0.4 | 8.74E-03 | 19.2 | 4.09E-02 | 90.1 | 1.07E-01 | 234.4 |
| 7 | 0.0440 | | | 2.41E-02 | 54.8 | 2.24E-02 | 50.9 | 1.33E-04 | 0.3 | 8.13E-03 | 18.5 | 4.76E-02 | 108.2 | 1.08E-01 | 245.7 |
| 8 | 0.0451 | | | 2.34E-02 | 51.9 | 2.48E-02 | 55.1 | 1.73E-04 | 0.4 | 8.23E-03 | 18.2 | 4.89E-02 | 108.3 | 1.11E-01 | 246.9 |
| Ave | 0.0448 | | | 2.45E-02 | 54.6 | 2.40E-02 | 53.7 | 1.63E-04 | 0.4 | 8.19E-03 | 18.3 | 4.60E-02 | 102.8 | 1.09E-01 | 242.8 |
| 9 | 0.0431 | | | 1.75E-02 | 40.6 | 3.99E-03 | 9.2 | 1.31E-04 | 0.3 | 7.66E-04 | 1.8 | 1.78E-02 | 41.3 | 4.59E-02 | 106.3 |
| 10 | 0.0449 | | | 1.83E-02 | 40.8 | 4.17E-03 | 9.3 | 1.29E-04 | 0.3 | 7.96E-04 | 1.8 | 1.79E-02 | 39.8 | 4.71E-02 | 104.9 |
| 11 | 0.0439 | | | 1.81E-02 | 41.1 | 4.36E-03 | 10.0 | 1.29E-04 | 0.3 | 7.44E-04 | 1.7 | 1.85E-02 | 42.0 | 4.75E-02 | 108.1 |
| 12 | 0.0450 | | | 1.82E-02 | 40.4 | 3.86E-03 | 8.6 | 1.34E-04 | 0.3 | 7.68E-04 | 1.7 | 1.85E-02 | 41.0 | 4.73E-02 | 105.1 |
| Ave | 0.0442 | | | 1.80E-02 | 40.7 | 4.10E-03 | 9.3 | 1.31E-04 | 0.3 | 7.70E-04 | 1.7 | 1.82E-02 | 41.0 | 4.69E-02 | 106.1 |
| Adjusted to 100% ------> | | | 12.3 | | 38.4 | | 8.7 | | 0.3 | | 1.6 | | 38.7 | | 100.0 |

## Table 5.11 TRA Warm Waste Pond - Sequential Extraction Iron Dissolution, All data in grams

| Sample No. | Initial Iron | Ion-X Iron Released | % diss | CO3 Iron Released | % diss | MnOx Iron Released | % diss | FeOx Iron Released | % diss | Organic Iron Released | % diss | Lattice Iron Released | % left | Iron Released | Mass Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0451 | 1.54E-05 | 0.0 | | | | | | | | | | | | |
| 2 | 0.0455 | 9.24E-06 | 0.0 | | | | | | | | | | | | |
| 3 | 0.0451 | 8.46E-06 | 0.0 | | | | | | | | | | | | |
| Ave | 0.0452 | 1.10E-05 | 0.0 | | | | | | | | | | | | |
| 5 | 0.0463 | | | 3.92E-04 | 0.8 | 1.96E-03 | 4.2 | 1.28E-02 | 27.6 | 4.98E-05 | 0.1 | 4.70E-02 | 101.4 | 6.22E-02 | 134.2 |
| 6 | 0.0473 | | | 3.92E-04 | 0.8 | 1.59E-03 | 3.4 | 1.24E-02 | 26.2 | 1.69E-05 | 0.0 | 3.88E-02 | 82.0 | 5.32E-02 | 112.5 |
| 7 | 0.0458 | | | 3.62E-04 | 0.8 | 1.63E-03 | 3.6 | 1.25E-02 | 27.4 | 1.74E-05 | 0.0 | 4.85E-02 | 106.0 | 6.31E-02 | 137.8 |
| 8 | 0.0470 | | | 3.36E-04 | 0.7 | 1.76E-03 | 3.8 | 1.30E-02 | 27.6 | 2.20E-05 | 0.0 | 5.01E-02 | 106.8 | 6.52E-02 | 138.9 |
| Ave | 0.0466 | | | 3.71E-04 | 0.8 | 1.74E-03 | 3.7 | 1.27E-02 | 27.2 | 2.73E-05 | 0.1 | 4.61E-02 | 99.1 | 6.09E-02 | 130.9 |
| 9 | 0.0449 | | | 3.36E-04 | 0.7 | 2.81E-03 | 6.3 | 9.16E-03 | 20.4 | 5.33E-04 | 1.2 | 3.15E-02 | 70.2 | 4.44E-02 | 98.8 |
| 10 | 0.0467 | | | 3.71E-04 | 0.8 | 2.23E-03 | 4.8 | 9.60E-03 | 20.5 | 1.15E-03 | 2.5 | 3.13E-02 | 66.9 | 4.46E-02 | 95.4 |
| 11 | 0.0457 | | | 3.43E-04 | 0.7 | 2.56E-03 | 5.6 | 9.12E-03 | 19.9 | 9.30E-04 | 2.0 | 3.20E-02 | 70.0 | 4.50E-02 | 98.3 |
| 12 | 0.0468 | | | 3.64E-04 | 0.8 | 3.43E-03 | 7.3 | 9.30E-03 | 19.9 | 5.75E-04 | 1.2 | 3.20E-02 | 68.3 | 4.57E-02 | 97.5 |
| Ave | 0.0461 | | | 3.54E-04 | 0.8 | 2.75E-03 | 6.0 | 9.30E-03 | 20.2 | 7.96E-04 | 1.7 | 3.17E-02 | 68.8 | 4.49E-02 | 97.5 |
| Adjusted to 100% ------> | | | 0.0 | | 0.8 | | 6.1 | | 20.7 | | 1.8 | | 70.6 | | 100.0 |

## Table 5.12 TRA Warm Waste Pond - Sequential Extraction Manganese Dissolution, All data in grams

| Sample No. | Initial Manganese | Ion-X Manganese Released | % diss | CO3 Manganese Released | % diss | MnOx Manganese Released | % diss | FeOx Manganese Released | % diss | Organic Manganese Released | % diss | Lattice Manganese Released | % left | Manganese Released | Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0025 | 5.87E-06 | 0.2 | | | | | | | | | | | | |
| 2 | 0.0025 | 6.24E-06 | 0.2 | | | | | | | | | | | | |
| 3 | 0.0025 | 7.68E-06 | 0.3 | | | | | | | | | | | | |
| Ave | 0.0025 | 6.60E-06 | 0.3 | | | | | | | | | | | | |
| 5 | 0.0025 | | | 7.20E-04 | 28.3 | 1.99E-03 | 78.3 | 1.04E-03 | 41.0 | 5.86E-05 | 2.3 | 2.30E-03 | 90.5 | 6.13E-03 | 240.7 |
| 6 | 0.0026 | | | 6.90E-04 | 26.5 | 2.02E-03 | 77.8 | 1.45E-03 | 55.6 | 1.56E-04 | 6.0 | 2.11E-03 | 81.0 | 6.43E-03 | 247.2 |
| 7 | 0.0025 | | | 6.84E-04 | 27.2 | 1.82E-03 | 72.3 | 1.18E-03 | 46.7 | 1.02E-04 | 4.1 | 2.37E-03 | 94.1 | 6.15E-03 | 244.6 |
| 8 | 0.0026 | | | 7.06E-04 | 27.4 | 2.03E-03 | 78.9 | 1.06E-03 | 41.2 | 1.09E-04 | 4.2 | 2.40E-03 | 93.1 | 6.32E-03 | 245.1 |
| Ave | 0.0026 | | | 7.01E-04 | 27.4 | 1.97E-03 | 76.8 | 1.18E-03 | 46.1 | 1.06E-04 | 4.1 | 2.29E-03 | 89.7 | 6.26E-03 | 244.4 |
| 9 | 0.0025 | | | 7.74E-04 | 31.4 | 1.37E-03 | 55.7 | 9.78E-05 | 4.0 | 2.85E-05 | 1.2 | 6.65E-04 | 27.0 | 2.95E-03 | 119.4 |
| 10 | 0.0026 | | | 8.82E-04 | 34.4 | 1.29E-03 | 50.2 | 9.90E-05 | 3.9 | 3.19E-05 | 1.2 | 6.65E-04 | 25.9 | 2.97E-03 | 115.9 |
| 11 | 0.0025 | | | 7.32E-04 | 29.1 | 1.27E-03 | 50.6 | 9.60E-05 | 3.8 | 3.04E-05 | 1.2 | 6.73E-04 | 26.8 | 2.81E-03 | 111.8 |
| 12 | 0.0026 | | | 7.36E-04 | 28.7 | 1.25E-03 | 48.5 | 9.64E-05 | 3.8 | 2.86E-05 | 1.1 | 6.93E-04 | 26.9 | 2.81E-03 | 109.3 |
| Ave | 0.0025 | | | 7.82E-04 | 30.9 | 1.30E-03 | 51.3 | 9.78E-05 | 3.9 | 2.99E-05 | 1.2 | 6.74E-04 | 26.6 | 2.89E-03 | 114.1 |
| Adjusted to 100% ------> | | | 0.2 | | 27.1 | | 44.9 | | 3.4 | | 1.0 | | 23.3 | | 100.0 |

## Table 5.13 TRA Warm Waste Pond - Sequential Extraction Silicon Dissolution, All data in grams

| Sample No. | Initial Silicon | Ion-X Silicon Released | % diss | CO3 Silicon Released | % diss | MnOx Silicon Released | % diss | FeOx Silicon Released | % diss | Organic Silicon Released | % diss | Lattice Silicon Released | % left | Silicon Released | Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.5785 | 1.13E-04 | 0.0 | | | | | | | | | | | | |
| 2 | 0.5837 | 1.21E-04 | 0.0 | | | | | | | | | | | | |
| 3 | 0.5778 | 1.60E-04 | 0.0 | | | | | | | | | | | | |
| Ave | 0.5800 | 1.31E-04 | 0.0 | | | | | | | | | | | | |
| 5 | 0.5940 | | | 1.88E-03 | 0.3 | 1.88E-03 | 0.3 | 4.22E-03 | 0.7 | 2.08E-04 | 0.0 | 5.88E-01 | 96.9 | 5.96E-01 | 100.3 |
| 6 | 0.6067 | | | 2.32E-03 | 0.4 | 1.86E-03 | 0.3 | 3.48E-03 | 0.6 | 6.11E-04 | 0.1 | 4.99E-01 | 82.3 | 5.06E-01 | 83.7 |
| 7 | 0.5872 | | | 1.81E-03 | 0.3 | 1.84E-03 | 0.3 | 3.53E-03 | 0.6 | 6.49E-04 | 0.1 | 5.66E-01 | 96.3 | 5.74E-01 | 97.7 |
| 8 | 0.6020 | | | 1.82E-03 | 0.3 | 1.94E-03 | 0.3 | 3.63E-03 | 0.6 | 5.64E-04 | 0.1 | 5.51E-01 | 91.5 | 5.59E-01 | 92.8 |
| Ave | 0.5975 | | | 1.96E-03 | 0.3 | 1.88E-03 | 0.3 | 3.72E-03 | 0.6 | 5.08E-04 | 0.1 | 5.51E-01 | 92.3 | 5.59E-01 | 93.6 |
| 9 | 0.5757 | | | 1.87E-03 | 0.3 | 1.36E-03 | 0.2 | 1.90E-03 | 0.3 | 2.79E-03 | 0.5 | 5.46E-01 | 94.9 | 5.54E-01 | 96.3 |
| 10 | 0.5992 | | | 1.90E-03 | 0.3 | 1.30E-03 | 0.2 | 2.21E-03 | 0.4 | 5.26E-03 | 0.9 | 5.19E-01 | 86.6 | 5.30E-01 | 88.4 |
| 11 | 0.5864 | | | 1.73E-03 | 0.3 | 1.34E-03 | 0.2 | 1.89E-03 | 0.3 | 4.26E-03 | 0.7 | 4.89E-01 | 83.4 | 4.96E-01 | 85.0 |
| 12 | 0.6005 | | | 1.69E-03 | 0.3 | 1.34E-03 | 0.2 | 2.06E-03 | 0.3 | 2.53E-03 | 0.4 | 6.59E-01 | 109.8 | 6.67E-01 | 111.1 |
| Ave | 0.5904 | | | 1.79E-03 | 0.3 | 1.33E-03 | 0.2 | 2.01E-03 | 0.3 | 3.72E-03 | 0.6 | 5.53E-01 | 93.7 | 5.62E-01 | 95.2 |
| Adjusted to 100% -------> | | | 0.0 | | 0.3 | | 0.2 | | 0.4 | | 0.7 | | 96.4 | | 100.0 |

## Table 5.14 TRA Warm Waste Pond - Sequential Extraction Aluminum Dissolution, All data in grams

| Sample No. | Initial Aluminum | Ion-X Aluminum Released | % diss | CO3 Aluminum Released | % diss | MnOx Aluminum Released | % diss | FeOx Aluminum Released | % diss | Organic Aluminum Released | % diss | Lattice Aluminum Released | % left | Aluminum Released | Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0940 | 2.66E-05 | 0.0 | | | | | | | | | | | | |
| 2 | 0.0948 | 2.66E-05 | 0.0 | | | | | | | | | | | | |
| 3 | 0.0939 | 2.66E-05 | 0.0 | | | | | | | | | | | | |
| Ave | 0.0942 | 2.66E-05 | 0.0 | | | | | | | | | | | | |
| 5 | 0.0965 | | | 3.16E-05 | 0.0 | 6.84E-04 | 0.7 | 3.24E-03 | 3.4 | 4.34E-05 | 0.0 | 1.06E-01 | 110.0 | 1.10E-01 | 114.2 |
| 6 | 0.0966 | | | 2.90E-05 | 0.0 | 4.75E-04 | 0.5 | 3.19E-03 | 3.2 | 1.52E-05 | 0.0 | 6.64E-02 | 69.7 | 9.21E-02 | 93.5 |
| 7 | 0.0954 | | | 2.36E-05 | 0.0 | 4.16E-04 | 0.4 | 3.15E-03 | 3.3 | 1.70E-05 | 0.0 | 1.09E-01 | 113.8 | 1.12E-01 | 117.6 |
| 8 | 0.0978 | | | 2.36E-05 | 0.0 | 5.65E-04 | 0.6 | 3.22E-03 | 3.3 | 2.28E-05 | 0.0 | 1.07E-01 | 109.8 | 1.11E-01 | 113.7 |
| Ave | 0.0971 | | | 2.70E-05 | 0.0 | 5.40E-04 | 0.6 | 3.20E-03 | 3.3 | 2.46E-05 | 0.0 | 1.03E-01 | 105.8 | 1.06E-01 | 109.7 |
| 9 | 0.0935 | | | 2.36E-05 | 0.0 | 1.04E-03 | 1.1 | 1.77E-03 | 1.9 | 8.88E-04 | 0.9 | 8.95E-02 | 95.7 | 9.32E-02 | 99.7 |
| 10 | 0.0973 | | | 2.89E-05 | 0.0 | 7.92E-04 | 0.8 | 1.99E-03 | 2.0 | 1.74E-03 | 1.8 | 9.10E-02 | 93.5 | 9.56E-02 | 98.2 |
| 11 | 0.0953 | | | 2.36E-05 | 0.0 | 9.72E-04 | 1.0 | 1.81E-03 | 1.9 | 1.44E-03 | 1.5 | 9.06E-02 | 95.3 | 9.50E-02 | 99.7 |
| 12 | 0.0976 | | | 2.36E-05 | 0.0 | 9.90E-04 | 1.0 | 1.85E-03 | 1.9 | 8.26E-04 | 0.8 | 9.43E-02 | 96.6 | 9.60E-02 | 100.4 |
| Ave | 0.0959 | | | 2.51E-05 | 0.0 | 9.48E-04 | 1.0 | 1.86E-03 | 1.9 | 1.22E-03 | 1.3 | 9.14E-02 | 95.3 | 9.55E-02 | 99.5 |
| Adjusted to 100% -------> | | | 0.0 | | 0.0 | | 1.0 | | 1.9 | | 1.3 | | 95.7 | | 100.0 |

## Table 5.15 TRA Warm Waste Pond - Sequential Extraction Potassium Dissolution, All data in grams

| Sample No. | Initial Potassium | Ion-X Potassium Released | % diss | CO3 Potassium Released | % diss | MnOx Potassium Released | % diss | FeOx Potassium Released | % diss | Organic Potassium Released | % diss | Lattice Potassium Released | % left | Potassium Released | Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0378 | 9.9E-02 | 263 | (<----------KNO3 Brine used in all Extractions----------->) | | | | | | | | | | | |
| 2 | 0.0381 | 3.9E-02 | 103 | | | | | | | | | | | | |
| 3 | 0.0377 | 9.9E-02 | 263 | | | | | | | | | | | | |
| Ave | 0.0379 | 7.9E-02 | 210 | | | | | | | | | | | | |
| 5 | 0.0386 | | | -8.07E-02 | -208.1 | -4.08E-02 | -105.2 | -6.08E-02 | -156.7 | 2.03E-01 | 523.7 | 2.74E-01 | 706.8 | 3.76E-01 | 970.3 |
| 6 | 0.0396 | | | -8.07E-02 | -203.7 | -4.08E-02 | -103.0 | -6.08E-02 | -153.4 | 2.50E-01 | 631.5 | 3.09E-01 | 780.8 | 4.60E-01 | 1161.9 |
| 7 | 0.0383 | | | -2.07E-02 | -54.0 | -4.08E-02 | -106.4 | -6.08E-02 | -158.5 | 2.50E-01 | 652.4 | 3.13E-01 | 817.0 | 5.22E-01 | 1360.2 |
| 8 | 0.0393 | | | -2.07E-02 | -52.7 | -4.08E-02 | -103.8 | -6.08E-02 | -154.6 | 2.50E-01 | 636.4 | 3.13E-01 | 796.9 | 5.24E-01 | 1332.0 |
| Ave | 0.0390 | | | -5.07E-02 | -129.6 | -4.08E-02 | -104.6 | -6.08E-02 | -155.8 | 2.36E-01 | 611.0 | 3.02E-01 | 775.4 | 4.70E-01 | 1208.1 |
| 9 | 0.0376 | | | -8.07E-02 | -214.7 | -4.08E-02 | -108.5 | -6.08E-02 | -161.7 | 1.93E-02 | 51.4 | 4.50E-02 | 119.7 | -3.91E-02 | -104.1 |
| 10 | 0.0391 | | | -8.07E-02 | -206.3 | -4.08E-02 | -104.3 | -6.08E-02 | -155.4 | 7.93E-02 | 202.7 | 4.75E-02 | 121.4 | 2.66E-02 | 67.9 |
| 11 | 0.0383 | | | -2.07E-02 | -54.1 | -4.08E-02 | -106.6 | -6.08E-02 | -158.8 | 7.93E-02 | 207.2 | 4.50E-02 | 117.5 | 8.23E-02 | 215.0 |
| 12 | 0.0392 | | | 3.93E-02 | 100.2 | -1.01E-01 | -257.1 | -6.08E-02 | -155.0 | 7.93E-02 | 202.3 | 4.75E-02 | 121.1 | 8.68E-02 | 221.3 |
| Ave | 0.0386 | | | -3.57E-02 | -93.7 | -5.58E-02 | -144.1 | -6.08E-02 | -157.7 | 6.43E-02 | 165.9 | 4.62E-02 | 119.9 | 3.91E-02 | 100.0 |

## Table 5.16 TRA Warm Waste Pond - Sequential Extraction Sodium Dissolution, All data in grams

| Sample No. | Initial Sodium | Ion-X Sodium Released | % diss | CO3 Sodium Released | % diss | MnOx Sodium Released | % diss | FeOx Sodium Released | % diss | Organic Sodium Released | % diss | Lattice Sodium Released | % left | Sodium Released | Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0194 | 5.39E-05 | 0.3 | | | | | | | | | | | | |
| 2 | 0.0196 | 5.99E-05 | 0.3 | | | | | | | | | | | | |
| 3 | 0.0194 | 4.80E-05 | 0.2 | | | | | | | | | | | | |
| Ave | 0.0195 | 5.38E-05 | 0.3 (NaOAc Extractant) | | | | | | | | | | | | |
| 5 | 0.0199 | | | -4.04E-02 | -202.7 | 5.00E-05 | 0.3 | 7.60E-05 | 0.4 | 5.33E-05 | 0.3 | 2.29E-02 | 114.9 | -1.73E-02 | -86.7 |
| 6 | 0.0204 | | | -4.04E-02 | -198.5 | 5.00E-05 | 0.2 | 6.40E-05 | 0.3 | 6.74E-05 | 0.3 | 2.10E-02 | 102.9 | -1.92E-02 | -94.4 |
| 7 | 0.0197 | | | -4.04E-02 | -205.1 | 9.80E-05 | 0.5 | 5.60E-05 | 0.3 | 9.09E-05 | 0.5 | 2.30E-02 | 116.4 | -1.72E-02 | -87.1 |
| 8 | 0.0202 | | | -4.04E-02 | -200.0 | 6.20E-05 | 0.3 | 7.00E-05 | 0.3 | 8.15E-05 | 0.4 | 2.61E-02 | 129.1 | -1.41E-02 | -69.6 |
| Ave | 0.0201 | | | -4.04E-02 | -201.6 | 6.50E-05 | 0.3 | 6.70E-05 | 0.3 | 7.32E-05 | 0.4 | 2.32E-02 | 115.8 | -1.69E-02 | -84.5 |
| 9 | 0.0193 | | | -4.04E-02 | -209.2 | 6.56E-03 | 33.9 | 2.60E-05 | 0.1 | 2.06E-04 | 1.1 | 2.10E-02 | 108.6 | -1.26E-02 | -65.2 |
| 10 | 0.0201 | | | -4.04E-02 | -201.0 | 3.44E-03 | 17.1 | 2.80E-05 | 0.1 | 2.42E-04 | 1.2 | 2.20E-02 | 109.3 | -1.47E-02 | -73.0 |
| 11 | 0.0197 | | | -4.04E-02 | -205.4 | 3.56E-03 | 18.1 | 3.40E-05 | 0.2 | 2.30E-04 | 1.2 | 2.22E-02 | 112.9 | -1.43E-02 | -72.7 |
| 12 | 0.0202 | | | -4.04E-02 | -200.5 | 6.56E-03 | 32.5 | 2.20E-05 | 0.1 | 2.12E-04 | 1.1 | 2.25E-02 | 111.5 | -1.11E-02 | -55.0 |
| Ave | 0.0198 | | | -4.04E-02 | -204.0 | 5.03E-03 | 25.4 | 2.80E-05 | 0.1 | 2.22E-04 | 1.1 | 2.19E-02 | 110.6 | -1.32E-02 | -66.5 |

## Table 5.17 TRA Warm Waste Pond - Sequential Extraction Carbonate Dissolution, All data in grams

| Sample No. | Initial Carbonate | Ion-X Carbonate Released | % diss | CO3 Carbonate Released | % diss | MnOx Carbonate Released | % diss | FeOx Carbonate Released | % diss | Organic Carbonate Released | % diss | Lattice Carbonate Released | % left | Carbonate Released | Closure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0060 | 3.31E-04 | 5.6 | | | | | | | | | | | | |
| 2 | 0.0060 | 5.53E-04 | 9.2 | | | | | | | | | | | | |
| 3 | 0.0059 | 3.93E-04 | 6.6 | | | | | | | | | | | | |
| Ave | 0.0060 | 4.26E-04 | 7.1 | | | | | | | | | | | | |
| 5 | 0.0061 | | | no detect | 88.1 | no detect | 96.7 | 6.24E-04 | 10.2 | 1.25E-04 | 2.0 | no detect | --- | --- | --- |
| 6 | 0.0062 | | | in extract | 88.1 | in extract | 96.7 | 4.12E-04 | 6.6 | 1.15E-04 | 1.8 | in extract | --- | --- | --- |
| 7 | 0.0060 | | | because of | 88.1 | because of | 96.7 | 5.06E-04 | 8.4 | 6.35E-05 | 1.1 | because | --- | --- | --- |
| 8 | 0.0062 | | | CO2 evolve | 88.1 | CO2 evolve | 96.7 | 2.05E-04 | 3.3 | 7.66E-05 | 1.2 | CO2 evolves a | --- | --- | --- |
| Ave | 0.0061 | | | --- | 88.1 | --- | 96.7 | 4.37E-04 | 7.1 | 9.49E-05 | 1.5 | | --- | --- | --- |
| 9 | 0.0059 | | | release | 81.0 | release | 10.6 | 2.62E-04 | 4.4 | 3.06E-04 | 5.2 | no detect | --- | --- | 106.7 |
| 10 | 0.0062 | | | based on | 81.0 | based on | 10.6 | 4.14E-04 | 6.7 | 4.66E-04 | 7.6 | in extract | --- | --- | 115.1 |
| 11 | 0.0060 | | | residue | 81.0 | residue | 10.6 | 4.80E-04 | 8.0 | 3.18E-04 | 5.3 | because | --- | --- | 111.4 |
| 12 | 0.0062 | | | analysis | 81.0 | analysis | 10.6 | 2.64E-04 | 4.3 | 4.16E-04 | 6.7 | CO2 evolves a | --- | --- | 109.7 |
| Ave | 0.0061 | | | --- | 81.0 | --- | 10.6 | 3.55E-04 | 5.8 | 3.77E-04 | 6.2 | | --- | --- | 110.7 |

Table Notes:

A) Samples 1-4 carried through all extractions to obtain progressive weight loss values.

B) Samples 5-8 were fresh samples for each extraction to determine if the extractant would dissolve the material removed by prior extractions. For simplicity, the initial and final weights have been omitted, and only the average initial weights are shown producing an error of less than 5%.

C) Samples 9-12 carried through all extractions to obtain progressive decontamination and matrix dissolution data.

D) The average weight loss, decontamination, and dissolution data measured for samples 1-3 were extrapolated to samples 5-12 to estimate the closure for each sample.

E) Initial contamination or matrix element values are estimated based on sample weight and the average sample assay.

F) Samples 2 and 3 were lost during the organic digestion step due to a violent reaction between the 30% hydrogen peroxide and the sample.

variability is well within the precision defined by the elemental analyses, reflecting the inherent heterogeneity of natural soils.

About half the total cesium released was by simple ion exchange, with the remainder distributed among the organic, iron oxide, carbonate, and manganese oxide phases in order of decreasing significance, (Figure 5.58). The remaining cesium may be in fine clay particles caught in surface microfissures which cannot be sufficiently contacted by extractants, or actually immobilized in insoluble silicate structures. The first explanation is more likely because it does not require significant solid-phase diffusion, and fine clay particles could certainly have been deposited in cracks over 40 years of pond operation.

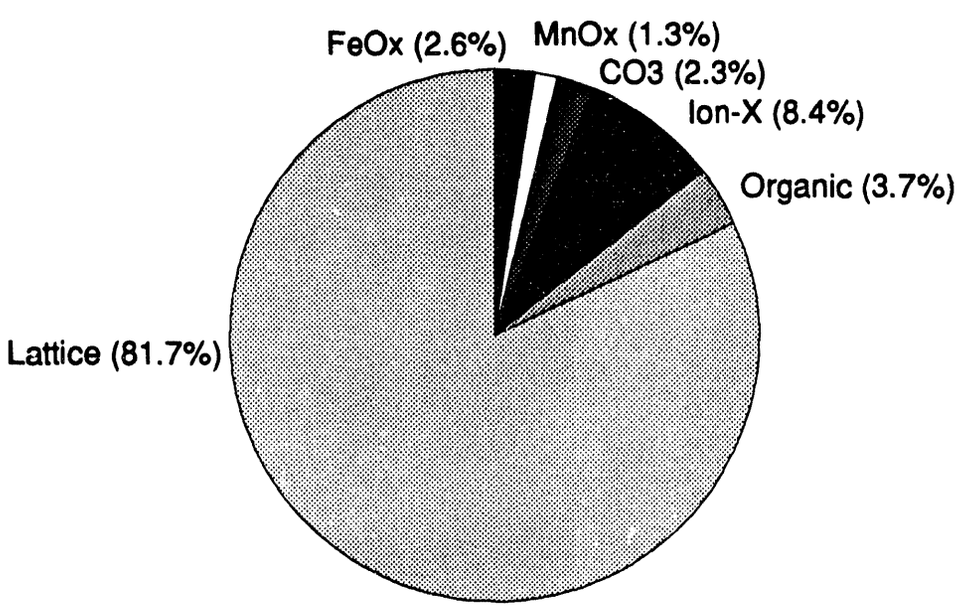


Figure 5.58 Cesium Distribution by Phase.

Over three-quarters of the cobalt released was attributed to the manganese oxide phase, the balance distributed amongst the iron oxide, carbonate and organic phases in order of decreasing significance (Figure 5.59). No cobalt was detected in solution

following the ion-exchange step.

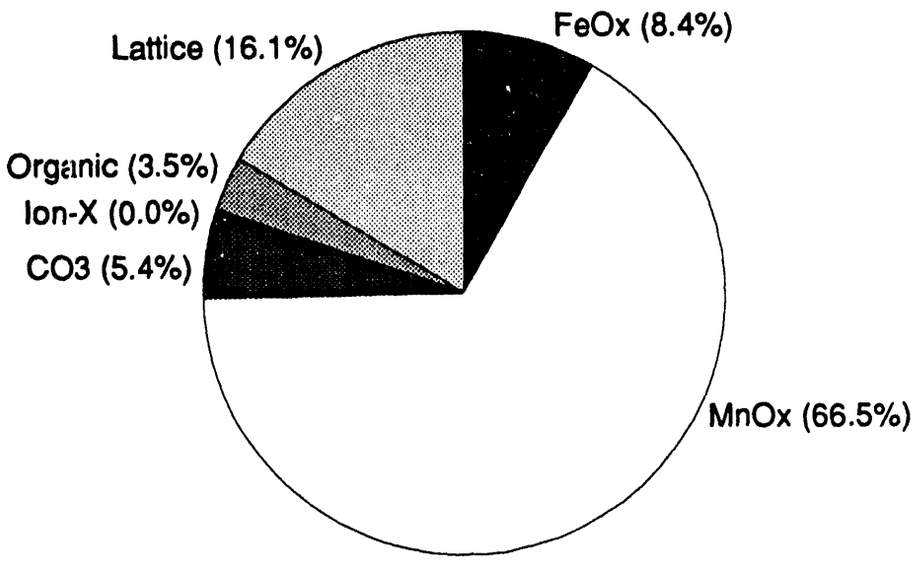


Figure 5.59 Cobalt Distribution by Phase.

The small amount of silicon and aluminum found in the sequential extractants confirms the intended negligible attack on the lattice. Comparing these results to the reported 80% recovery of cesium in a preliminary evaluation of extraction with hot acid, it can only be concluded that the hot acid actually etches the underlying silicate mineral surface - partially digesting the mineral grain to release the sorbed contamination.

3. Chromium Release

Over 90% of the chromium in the sample is extractable. About 57% of the total chromium contamination in the sample is released from the iron oxide phase. The organic phase also contributes a significant fraction (21%), followed by the carbonate and manganese oxide phases, with no significant release in the ion exchange extraction. The mass closure on chromium was uniformly over 100% for all samples,

indicating the initial assay was probably low. Figure 5.60 illustrates the distribution adjusted to 100%.

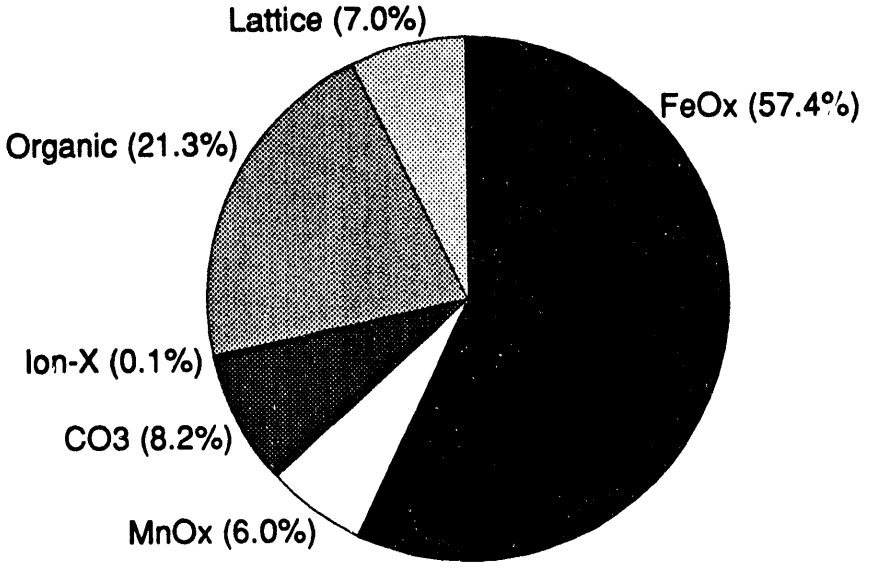


Figure 5.60 Chromium Distribution by Phase.

D. Extraction Specificity and Completeness

The designed extraction sequence is arranged with progressively more aggressive chemistry with the understanding that succeeding steps will complete the dissolution of any residual from a prior step as well as attacking the targeted phase. This expected result can be seen in the dissolution tables; new (unexposed) samples (numbers 5-8 in the tables) typically released more contaminant than previously exposed samples (numbers 9-12 in the tables). However, in many cases the release from new samples was not as much as all prior steps combined, and in some cases, the

previously exposed samples actually released more material than the new samples. It appears that though there is large overlap between the carbonate, manganese, and iron extractions, there is some fraction of each phase specifically dissolved only by the intended extractant. This

apparent chemical specificity may also be explained by the overlapping layers of the three phases and the sequence in which they are removed. The carbonate and metal oxide phases all form gradually over time due to mineral weathering. Possibly one extraction makes more of another phase available to a later extraction by removing a surface film or an intermixed phase (causing surface porosity).

All extractions should remove the ion exchangeable material because of the addition of brine to preclude resorption. The potassium release data (Table 5.15) includes many negative values, indicating significant increase in sample potassium concentration as potassium actively sorbs in exchange for other cations. Similarly the sodium release data shows negative values because the carbonate extraction is done with a sodium acetate solution which makes large amounts of sodium available for ion exchange. The concentrations of sodium and potassium were so high and the amounts exchanged so minor, that this tabular data should be evaluated for trend only. This is apparent in the potassium data for the ion-exchange step which indicates an impossible greater than 200% release from the sample. The residue (Table 5.18) verifies the actual increase in potassium content after exposure.

Table 5.18 TRA Warm Waste Pond - Single Extraction Residue Analyses
All data in grams, except Cs and Co in dps

| Species | Initial Assay | Ion-X Residual Content | % diss | CO3 Residual Content | % diss | MnOx Residual Content | % diss | FeOx Residual Content | % diss | Organic Residual Content | % diss |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cr | 0.0066 | 6.64E-03 | -0.6 | 7.02E-03 | -6.4 | 7.13E-03 | -8.1 | 1.34E-03 | 79.8 | 4.57E-03 | 30.8 |
| Cs | 3255 | 3.81E+03 | -17.2 | 3.92E+03 | -20.5 | 3.54E+03 | -8.7 | 3.55E+03 | -9.1 | 2.51E+03 | 22.7 |
| Co | 656 | 6.56E+02 | -0.0 | 7.85E+02 | -19.5 | 2.46E+02 | 62.5 | 4.71E+02 | 28.2 | 6.64E+02 | -1.1 |
| Ca | 0.0427 | 3.87E-02 | 9.3 | 2.50E-02 | 41.6 | 2.30E-02 | 46.2 | 4.71E-02 | -10.3 | 3.78E-02 | 11.5 |
| Fe | 0.0445 | 4.70E-02 | -5.8 | 5.17E-02 | -16.2 | 5.23E-02 | -17.6 | 3.66E-02 | 17.6 | 4.61E-02 | -3.7 |
| Mn | 0.0024 | 2.27E-03 | 7.1 | 2.07E-03 | 15.4 | 6.09E-04 | 75.1 | 1.54E-03 | 36.9 | 2.20E-03 | 9.9 |
| Si | 0.5702 | 5.18E-01 | 9.1 | 5.60E-01 | 1.7 | 5.65E-01 | 0.8 | 5.26E-01 | 7.8 | 5.50E-01 | 3.5 |
| Al | 0.0926 | 7.06E-02 | 23.8 | 9.20E-02 | 0.7 | 9.45E-02 | -2.0 | 8.76E-02 | 5.4 | 1.03E-01 | -10.7 |
| Na | 0.0372 | 2.04E-02 | 45.2 | 2.25E-02 | 39.7 | 2.20E-02 | 40.8 | 1.95E-02 | 47.5 | 2.32E-02 | 37.7 |
| K | 0.0191 | 4.50E-02 | -134.8 | 4.99E-02 | -160.6 | 4.48E-02 | -134.0 | 4.54E-02 | -136.9 | 6.41E-02 | -234.8 |
| C-org | 0.0517 | 6.06E-02 | -17.3 | 7.85E-02 | -51.9 | 5.82E-02 | -12.6 | 5.57E-02 | -7.8 | 4.43E-02 | 14.2 |
| CO3 | 0.0059 | 4.97E-03 | 15.3 | 6.96E-04 | 88.1 | 7.66E-05 | 98.7 | 3.86E-05 | 99.3 | 4.65E-03 | 20.7 |

The ion-exchange step not only provides the primary decontamination step for cesium, but also releases significant calcium (13%) from the matrix. The carbonate data in Table 5.17 indicates this is due to partial dissolution of that phase as well as ion-exchange, because about 7% of the carbonate is also released into solution. No effect is apparent on chromium, cobalt or any of the soil matrix constituents. The metals are apparently bound as oxides rather than exchangeable ions.

The carbonate extraction only removes an additional 40% of the total calcium from the matrix, but the carbonate in the residue is diminished a further 80%. This is a good example of the difference between available material and that bound in the unweathered mineral. Only 10% of the carbonate is left in the sample, but close to half of the calcium is still bound. The remainder of the carbonate may well have been extractable, but as described in the time study, the extraction was terminated after 24 hours because of the attack indicated on the easily-reducible phase. The data in Table 5.12 indicates 30% of the total manganese, (50% of the extractable content) was also dissolved. This release is attributed to lack of specificity, but some of the manganese may have been available in the carbonate phase rather than fixed to the underlying particle. Release data for the unextracted samples was comparable to the cumulative release for the ion exchange and carbonate extractions due to the presence of potassium brine as explained above.

The manganese-oxide and iron-oxide extractions complete the release of available material from prior steps as expected. The manganese step frees little iron, and neither cause significant attack on the underlying mineral. As with the calcium, fully 70% of the iron, and about 25% of the manganese is left in the mineral residue. It is believed this material is contained in the intact mineral lattice, but the experimental data cannot verify complete dissolution of the surface deposit.

The organic digestion alone (containing brine) released about as much material as the organic and ion exchange steps in the sequential extraction

combined. Little attack is indicated on any other phase. Calcium release is slightly greater which may be due to the nonspecific attack or the natural calcium content in biological material. Reduced iron extraction for the individual extraction compared to the sequential results may again be attributed to the diminished iron phase available due to covering by the other phases. Silicon and aluminum extraction is minimal, indicating negligible attack on the mineral matrix.

Analysis of the extraction residues was also limited by sample variability. The residue dissolutions were compared to complete digestions of unexposed samples to determine the percent dissolution in each step. The resulting number is therefore a calculated difference between two relatively large values with intrinsic variability. While the data is a good indication of gross effects, (i.e. the manganese extraction residue confirmed over 60% cobalt decontamination, with dissolution of half of the calcium and three-quarters of the manganese), more minor effects are masked by the data, and do not provide reliable confirmation of the extraction results.

## IV. CONCLUSIONS

On a purely chemical basis, over 90% of the chromium can be extracted from the -40 mesh material, and no doubt more easily from the larger material. Most of the cobalt can also be removed (84%), but with a half-life of only 5.271 years, a comparable reduction occurs naturally in less than 15 years. Cesium cannot be appreciably removed from the -40 mesh material by any practical soil washing flowsheet, because over 80% of the material (32,000 pCi/g in the -40 mesh sample) is bound in microfissures in the surface or in the silicate lattice itself and is unavailable to extraction.

The sequential extractions verify that significant recovery of available species can be achieved with less aggressive chemistry than boiling acid. This technique can provide an accurate account of contaminant distribution, with mass balances well within the precision of the soil matrix sample homogeneity.

Time studies to determine the required durations for extractions for a particular sample are essential for designing a study. The times used were significantly longer than those reported in the literature. Time-release profiles developed for cesium during the carbonate, manganese and iron extractions showed a strong tendency for rapid resorption. Tests with and without a potassium brine present to inhibit cesium resorption indicated extraction efficiency could be enhanced by as much as a factor of ten using the brine. Potassium selectivity for cesium displacement was apparent in the extraction results which showed a much stronger effect on cesium than on cobalt or chromium. These studies also allow identification of extraction complexities such as the procedure described above for conducting the organic digestion.

Soil washing cannot be practically applied to the Test Reactor Area Warm Waste Pond sediments to meet the criteria in the Record of Decision for cesium decontamination. The goals of 90% removal of contamination, and an average radionuclide content of 690 pCi/g cannot be accomplished for cesium by extractive soil washing. In addition, the waste generated by dissolution of 20% of the soil matrix caused by the test extractions would, if reconstituted, fill over 14,000 55-gallon drums requiring long-term management. Finally, the intrinsic risks of shipping and handling treatment chemicals, the worker exposure during excavation and processing, and the long-term exposure to workers managing the residuals offset much of the potential gains of decontaminating the soil.

## V. REFERENCES

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# APPENDIX A

# ELEMENTAL ANALYSIS TRIPLICATE DATA

Table A.1 Elemental Analysis Data (wt%)

| Aluminum | A | B | C | Ave. | Std Dev | % StdDev |
|---|---|---|---|---|---|---|
| +4 | | | | | | |
| +10 | 3.91 | 3.91 | 3.81 | 3.88 | 0.05 | 1.22 |
| +40 | 5.08 | 5.03 | 4.77 | 4.96 | 0.14 | 2.74 |
| +100 | 4.41 | 4.28 | 5.67 | 4.79 | 0.63 | 13.10 |
| +200 | 4.41 | 4.52 | 4.55 | 4.49 | 0.06 | 1.34 |
| +400 | 4.90 | 4.95 | 5.08 | 4.98 | 0.08 | 1.52 |
| -400 | 5.08 | 4.89 | 4.05 | 4.67 | 0.45 | 9.58 |

| Iron | A | B | C | Ave. | Std Dev | % StdDev |
|---|---|---|---|---|---|---|
| +4 | | | | | | |
| +10 | 1.27 | 1.14 | 1.31 | 1.24 | 0.07 | 5.85 |
| +40 | 1.58 | 1.71 | 1.59 | 1.63 | 0.06 | 3.63 |
| +100 | 1.79 | 1.63 | 1.69 | 1.70 | 0.07 | 3.87 |
| +200 | 2.18 | 2.86 | 2.91 | 2.65 | 0.33 | 12.56 |
| +400 | 3.40 | 2.29 | 2.28 | 2.66 | 0.53 | 19.79 |
| -400 | 2.96 | 3.05 | 3.01 | 3.01 | 0.04 | 1.22 |

| Chrome | A | B | C | Ave. | Std Dev | % StdDev |
|---|---|---|---|---|---|---|
| +4 | | | | | | |
| +10 | 0.017 | 0.017 | 0.016 | 0.02 | 0.000 | 1.29 |
| +40 | 0.069 | 0.078 | 0.063 | 0.07 | 0.006 | 8.26 |
| +100 | 0.132 | 0.133 | 0.129 | 0.13 | 0.002 | 1.29 |
| +200 | 0.331 | 0.337 | 0.389 | 0.35 | 0.026 | 7.39 |
| +400 | 0.351 | 0.369 | 0.379 | 0.37 | 0.012 | 3.16 |
| -400 | 0.669 | 0.677 | 0.552 | 0.63 | 0.057 | 9.03 |

| Manganese | A | B | C | Ave. | Std Dev | % StdDev |
|---|---|---|---|---|---|---|
| +4 | | | | | | |
| +10 | 0.017 | 0.017 | 0.017 | 0.02 | 0.000 | 0.72 |
| +40 | 0.039 | 0.042 | 0.029 | 0.04 | 0.006 | 15.14 |
| +100 | 0.053 | 0.052 | 0.054 | 0.05 | 0.001 | 1.63 |
| +200 | 0.118 | 0.131 | 0.145 | 0.13 | 0.011 | 8.39 |
| +400 | 0.133 | 0.132 | 0.136 | 0.13 | 0.002 | 1.27 |
| -400 | 0.209 | 0.207 | 0.172 | 0.20 | 0.017 | 8.67 |

| Silicon | A | B | C | Ave. | Std Dev | % StdDev |
|---|---|---|---|---|---|---|
| +4 | | | | | | |
| +10 | 30.1 | 31.2 | 32.1 | 31.13 | 0.818 | 2.63 |
| +40 | 31.0 | 32.7 | 29.6 | 31.10 | 1.268 | 4.08 |
| +100 | 31.0 | 31.5 | 28.9 | 30.47 | 1.126 | 3.70 |
| +200 | 23.5 | 23.0 | 21.6 | 22.70 | 0.804 | 3.54 |
| +400 | 27.3 | 24.4 | 26.2 | 25.97 | 1.195 | 4.60 |
| -400 | 23.2 | 22.8 | 21.4 | 22.47 | 0.772 | 3.43 |

Table A.1 Elemental Analysis Data (cont.)

| Calcium | A | B | C | Ave. | Std Dev | % StdDev |
|---|---|---|---|---|---|---|
| +4 | | | | | | |
| +10 | 2.51 | 2.35 | 2.48 | 2.45 | 0.069 | 2.84 |
| +40 | 1.00 | 1.09 | 0.92 | 1.00 | 0.069 | 6.88 |
| +100 | 1.53 | 1.23 | 1.56 | 1.44 | 0.149 | 10.35 |
| +200 | 2.73 | 3.52 | 3.47 | 3.24 | 0.361 | 11.15 |
| +400 | 3.95 | 2.81 | 2.83 | 3.20 | 0.533 | 16.67 |
| -400 | 2.13 | 2.27 | 2.07 | 2.16 | 0.084 | 3.89 |

| Organic C | A | B | C | Ave. | Std Dev | % StdDev |
|---|---|---|---|---|---|---|
| +4 | | | | | | |
| +10 | 0.219 | 0.246 | | 0.23 | 0.013 | 5.81 |
| +40 | 0.701 | 0.706 | | 0.70 | 0.002 | 0.36 |
| +100 | 1.430 | 1.490 | | 1.46 | 0.030 | 2.05 |
| +200 | 3.010 | 3.360 | | 3.19 | 0.175 | 5.49 |
| +400 | 3.790 | 3.950 | | 3.87 | 0.080 | 2.07 |
| -400 | 4.080 | 4.070 | | 4.08 | 0.005 | 0.12 |

| Inorg C | A | B | C | Ave. | Std Dev | % StdDev |
|---|---|---|---|---|---|---|
| +4 | | | | | | |
| +10 | 0.61 | 0.61 | | 0.61 | 0.000 | 0.00 |
| +40 | 0.06 | 0.05 | | 0.06 | 0.005 | 9.09 |
| +100 | 0.13 | 0.11 | | 0.12 | 0.010 | 8.33 |
| +200 | 0.67 | 0.68 | | 0.68 | 0.005 | 0.74 |
| +400 | 0.51 | 0.49 | | 0.50 | 0.010 | 2.00 |
| -400 | 0.37 | 0.38 | | 0.38 | 0.005 | 1.33 |

# APPENDIX B

## X-RAY DIFFRACTION PHASE LISTING

## Table B.1 X-ray Diffraction Data (wt%)

| Sieve Size | Quartz SiO2 | Calcite CaCO3 | Aragonite CaCO3 | KNaCO3 | Total CaCO3 | Total ++CO3 | Microcline KAlSi3O8 | Sanidine KAlSi3O8 | Orthoclase KAlSi3O8 | Total KAlSi3O8 | Albite NaAlSi3O8 | Total +AlSi3O8 | Anorthite CaAl2Si2O8 | CaAl2Si2O8-4H2O | Total CaAlSiO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| +4 | | | | | 0 | 0 | | | | 0 | | 0 | | | 0 |
| +10 | 41.7 | 11.1 | | | 11.1 | 11.1 | | | 6.5 | 6.5 | | 6.5 | | | 0 |
| +40 | 50.3 | | 3.6 | | 3.6 | 3.6 | | 4.7 | 6.9 | 11.6 | 8 | 19.6 | 16.2 | | 16.2 |
| +100 | 34.3 | | 4.5 | | 4.5 | 4.5 | | | 13.9 | 13.9 | | 13.9 | 13.1 | | 13.1 |
| +200 | 28.1 | | 4.5 | | 4.5 | 4.5 | | | 7.8 | 7.8 | | 7.8 | 8.5 | | 8.5 |
| +400 | 42.7 | | 2.9 | | 2.9 | 2.9 | | | 21.9 | 21.9 | | 21.9 | 9.1 | | 9.1 |
| -400 | 14.8 | 15.9 | 5.7 | 4.1 | 21.6 | 25.7 | 2.3 | | | 2.3 | | 2.3 | 8.1 | 11.7 | 19.8 |

| Pyrope Mg3Al2Si3O12 | Total ++AlSi3O8 | Ca3(SiO3(OH)2) | Total XXSixOy | CaTiSiO5 | CaH2P2O7 | (Fe,Mg)SiO3 | CaCrSi4O10 | Total ++XXX | Fe3O4 | Fe2O3 | MnO2 | Total FeMnOx | MgCrO4 | CrF2 | Total FeMnXX | Total FeMnCr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | | | | | | | 0 | | | | | | | | |
| 3 | 3 | | | 15.3 | 4.5 | | 8.1 | 42 | | | 3 | 3 | 6.8 | | 3 | 9.8 |
| | 16.2 | | | | | | | 19.8 | | | 1.2 | 1.2 | 9.9 | | 1.2 | 11.1 |
| | 13.1 | | | 6.7 | | 5.3 | | 29.6 | 5.9 | 2.7 | 1.1 | 9.7 | 13.5 | | 23.6 | 37.1 |
| 2.5 | 11 | | | 5 | | | 28.1 | 48.6 | | 2.5 | 2.1 | 4.6 | 13.3 | | 7.1 | 20.4 |
| | 9.1 | | | | | | | 12 | | 1.9 | 2 | 3.9 | 9.3 | 10.2 | 5.8 | 25.3 |
| | 19.8 | | 11.7 | 6.2 | | 10.5 | | 73.9 | | 3.2 | 4 | 7.2 | 8.2 | | 20.9 | 29.1 |

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