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Conf-9308137--8

Contaminant Resorption During Soil Washing

Dirk Gombert

Westinghouse Idaho Nuclear Company, Inc.
for the U.S. Department of Energy
Contract DE-AC07-84ID12435

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Prepared for Presentation at the
AIChE 1993 Summer National Meeting
August 15-19, 1993

Session 50: New Techniques for Soil Remediation

Westinghouse Idaho Nuclear Company, Inc.

ABSTRACT

To evaluate the applicability of soil washing to a specific site, requires some basic research in how contaminants are bound. Much can be learned from sequential extraction methodology based on micronutrient bioavailability studies wherein the soil matrix is chemically dissected to selectively remove particular fixation mechanisms independently. This procedure uses a series of progressively more aggressive solvents to dissolve the principle phases that make up a soil, 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. This physical model assumes no ion exchange or adsorption at sites either previously occupied by other ions, or exposed by the dissolution. Therefore, to make engineering use of the sequential extraction data, the release of contamination must be evaluated relative to the effects of resorption. Time release studies were conducted to determine the optimum duration for extraction to maximize complete destruction of the target matrix fraction while minimizing contaminant 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.

I. INTRODUCTION

Soil washing is one technique used to reduce the volume of contaminated soils requiring further treatment or continued management (EPA, Engineering..., 1989 and Innovative..., 1990). While the technology has been demonstrated for organics and to some extent for metals, adapting the technology to mixed-waste soils (radionuclide contaminated soils containing other hazardous constituents) presents a significant challenge. The contaminants are not limited to transition and heavy metals, but also include alkali and alkaline earth fission products

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that are chemically analogous to natural soil constituents which make up percent levels of the soil matrix. To develop an adequate knowledge base to definitively judge the applicability of the technology, requires some basic research in how contaminants are bound, so flowsheets can be targeted at controlling mechanisms, (Gombert and Bosley, 1992).

Much can be learned from sequential extraction methodology based on micronutrient bioavailability studies wherein the soil matrix is chemically dissected to selectively dissolve particular fixation mechanisms independently (Calmano and Forstner, 1983, Tessier, et al., 1979, Gibson and Farmer, 1986, and Salomons and Forstner, 1980). 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.

Reviews of soil washing as currently applied, particularly in Europe, indicate a general acceptance that fine particulate present in solution resorb extracted contaminants. Wet screening is used to remove particulate below a 63 to 74 micron cutoff range, which is then disposed of as hazardous waste. Though chemical extraction may be employed in conjunction with screening, soils containing more than 10-20% fines below the cutoff size, are generally not cost effectively treated with soil washing (PFEIFFER, et. al., 1990, EPA, Cleaning..., 1989, and EPA, Assessment..., 1988). 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 the six typically principle phases that make up a soil: 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. 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 is, in effect, assuming no ion exchange or adsorption at sites either previously occupied by other ions, or exposed by the dissolution.

It is typical in the referenced studies, 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. 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 (Rendell et. al., 1980).

B. Research Need

Ideally, if one were characterizing a spill of limited extent, such that uncontaminated material of a similar nature were 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. That 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 (Perry, et. al., 1972). 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 (Perry, 1972, and Williams, 1953). 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 (Gibbs, 1977, Jenne, 1968, and Dragun, 1988). 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:

$$dC(\text{Fe})/dt = kAC(\text{solvent}),$$

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:

$$C(\text{Fe}) = kt + C_0(\text{Fe}), \text{ where } C_0(\text{Fe}) = C(\text{Fe}) @ t=0$$

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:

$$dC(\text{Cs})/dt = -k'C(\text{Cs})$$

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:

$$C(\text{Cs}) = C_0(\text{Cs})\exp(-k't), \text{ where } C_0(\text{Cs}) = C(\text{Cs}) @ t=0$$

This equation may be used for the period following complete destruction of the iron oxide film, using the cesium concentration for C_0 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:

$$dC(\text{Cs})/dt = k - k'C(\text{Cs})$$

Integrating now yields:

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

Evaluating the integration constant with boundary condition $C_0(\text{Cs}) = 0$, results in:

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

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

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 1. Cesium concentration increases throughout the duration of the iron-oxide layer dissolution, then resorbs on the residue as long as sites are available.

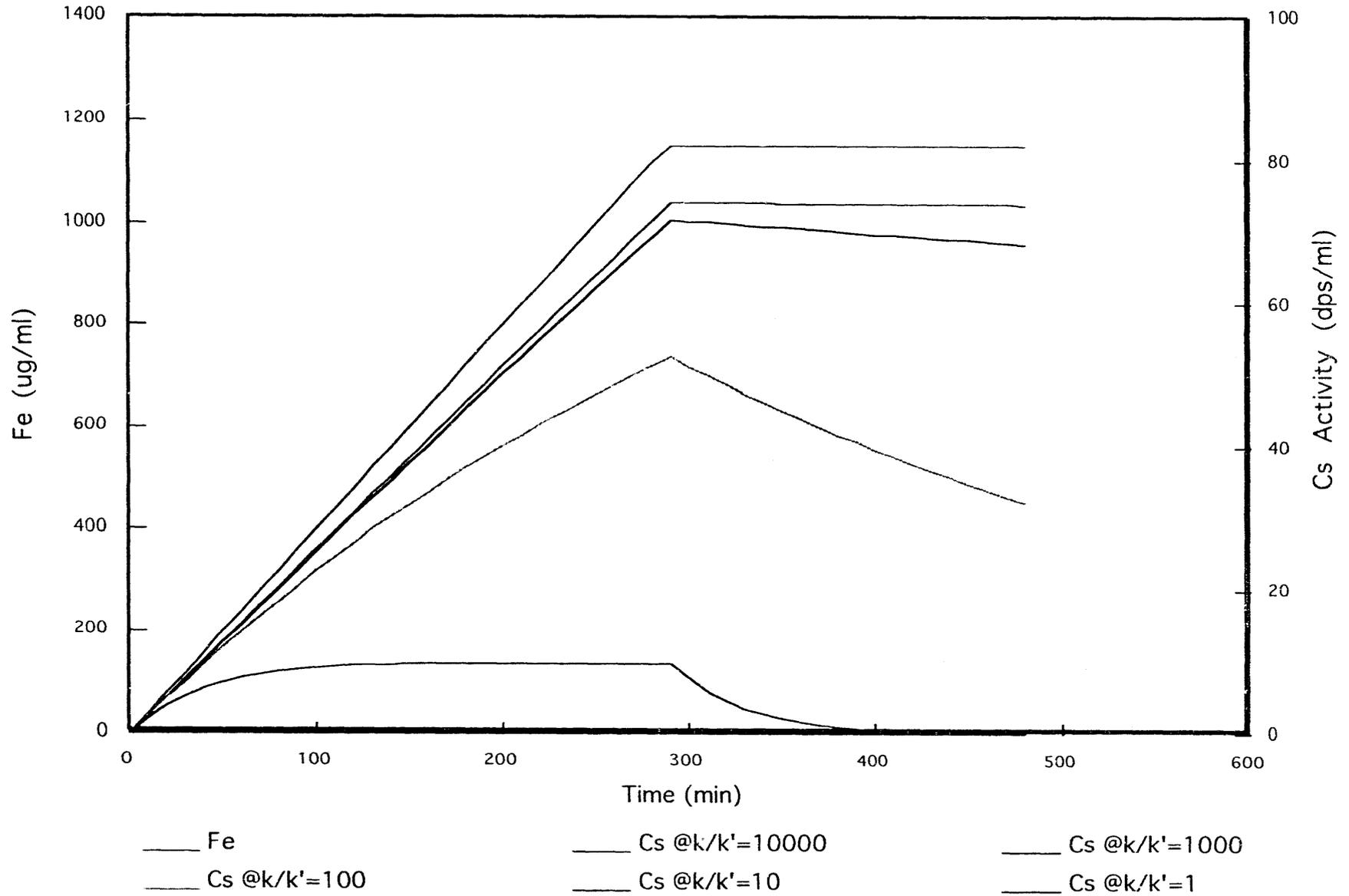
Without the counter-ion brine present, the combination of potassium's similar ionic size and much greater concentration should virtually preclude cesium resorption and significantly reduce cobalt and chromium resorption. It is unlikely that the ideal profiles based on such a simple model will be realized by experimental data. For example, if resorption occurs rapidly, and the sorption capacity is exceeded, the solution analyses will only show 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. The relative shapes, slopes, time-to-plateau, and magnitude of the profiles, should give an indication of the relative rates of release and resorption, (i.e. $k' \geq k$, $k' < k$, or $k' \ll k$) as shown in the hypothetical curves in Figure 1.

IV. EXPERIMENTAL DESIGN

A. Sample and Method

The sample used was an alluvial sediment deposited by the Big Lost River on the Snake River Plain within the boundaries of the Idaho National Engineering

Figure 1. Relative Rates of Dissolution (k) vs. Readsorption (k')
 Fe (matrix dissolved) and Cs (contaminant released)



Laboratory (INEL). The material was contaminated over a period of several decades by the outfall of cooling water containing chromium corrosion inhibitor and trace amounts of radionuclides including cesium. The soil is a poorly sorted mixture of volcanic origin, approximately 40 wt% of which is below 4 mesh.

Rate studies were conducted to qualitatively determine the relative significance of resorption versus dissolution and contaminant release. Steps 2, 3, and 4 of the extraction sequence were characterized by measuring net contaminant release with and without a counter-ion present for increasing periods of soil/extractant contact. For example, as the moderately-reducible metal-oxide fraction of the soil matrix (mainly crystalline oxides of iron) was destroyed in the sequential extraction, the concentration of iron, chromium, and the cesium activity in solution were measured to monitor the dissolution of the phase and the release of contaminants. The occurrence of a radionuclide with a high-energy gamma-decay (Cs^{137}) provides the opportunity to monitor incremental changes in concentration at six orders of magnitude lesser concentration than a typical elemental determination. Cesium is an ideal contaminant to monitor because it is known to interact with a silicate matrix such as clay and the exchangeable fraction sorbs in a manner similar to potassium which is relatively well documented (McHenry, 1954, Schulz, 1963, Nishita, et. al., 1960, and Miller and Reitmeier, 1963). Where iron concentration was used to track the rate of dissolution of the moderately-reducible metal oxide phase, the carbonate and readily-reducible metal oxide phases were monitored using calcium and manganese respectively. 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 (Poole and Schuette, 1985, Stumm and Morgan, 1981, and Buckman and Brady, 1969).

B. Procedure

The actual laboratory procedure used 400 grams of the -40 mesh soil fraction extracted first with 1 M potassium nitrate solution at pH 7 and room temperature, shaken for 2 hours to remove readily ion-exchangeable contamination. The time study data was generated as follows.

1. Carbonate Phase

Twenty samples of 5 grams each were extracted using 100 ml of 1 M sodium acetate adjusted to pH 5 with acetic acid. Sufficient potassium nitrate was added to half the solutions to make the mixtures one molar in potassium. The extractions were shaken at room temperature, and one sample was removed from each set of ten after 5, 10, and 30 minutes, 1, 2, 4, 6, 12, 18, and 24 hours. The pH was checked each hour and adjusted to pH 5 using acetic acid to control drift within 0.5 pH units.

All samples were centrifuged, rinsed twice with distilled water, and the total leachates analyzed for the Ca, Fe, Mn, Cr, Cs, and Co.

Three hundred grams of soil was extracted using the same liquid/solid ratio and the most effective extractant/time combination.

2. Easily Reducible Phase

From the 300 grams of material contacted above, 20 samples were extracted using the timed procedure described above, each using 100 ml of 0.1 M hydroxylamine hydrochloride acidified to pH 2 with 0.01 M nitric acid. The remaining 200 grams of bulk solids were extracted using the most effective extractant/time combination.

3. Moderately Reducible Phase

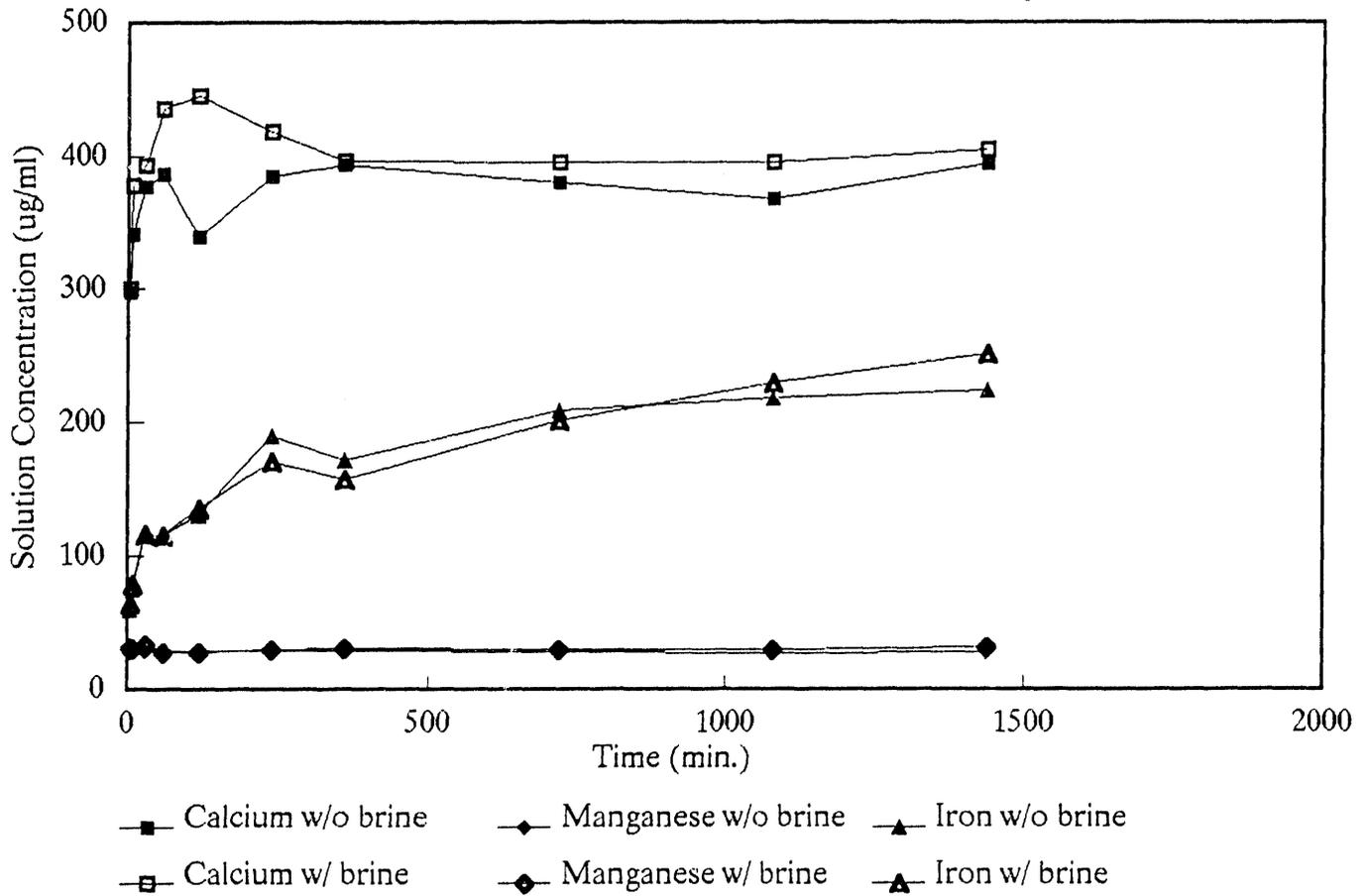
From the 200 grams of material contacted above, 20 samples were extracted again using the same timed procedure, but using 0.2 M ammonium oxalate acidified to pH 3 with 0.2 M oxalic acid.

V. RESULTS and DISCUSSION

The first mechanistic assumption necessary for analyzing the applicability of the model is that the matrix element chosen to monitor the progress of the dissolution is relatively unaffected by resorption (e.g. the extractant is effective not only in dissolving a phase, but in keeping it in solution). The

Matrix Element Time Release Profile

With and Without KNO₃ Brine to Control Resorption

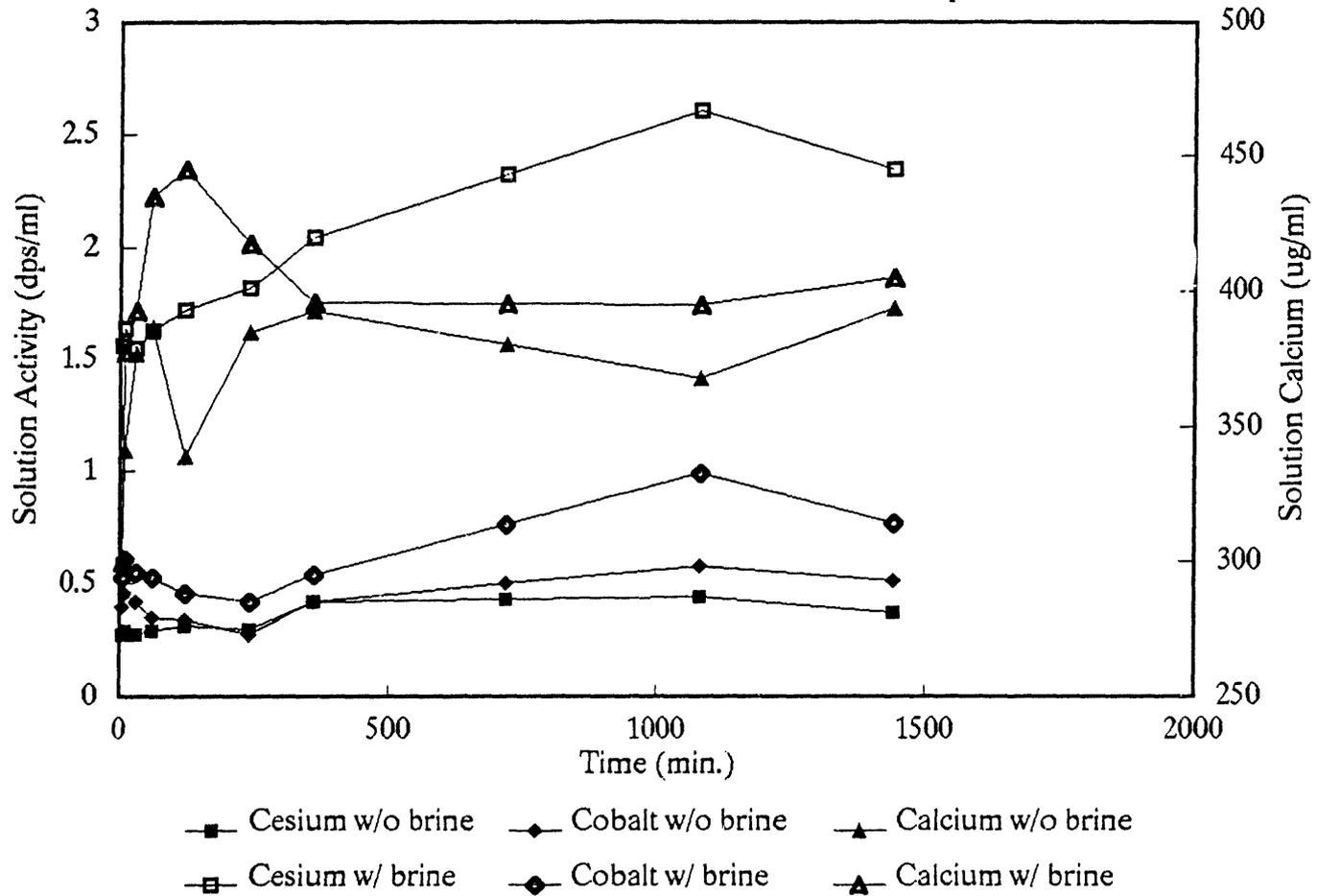


profiles for calcium during the carbonate extraction, manganese for the easily-reducible metal-oxide extraction, and iron for the moderately-reducible metal-oxide extraction are shown in Figure 2. Initial calcium release appears to be accelerated by the brine, but the time-to-plateau and steady-state 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.

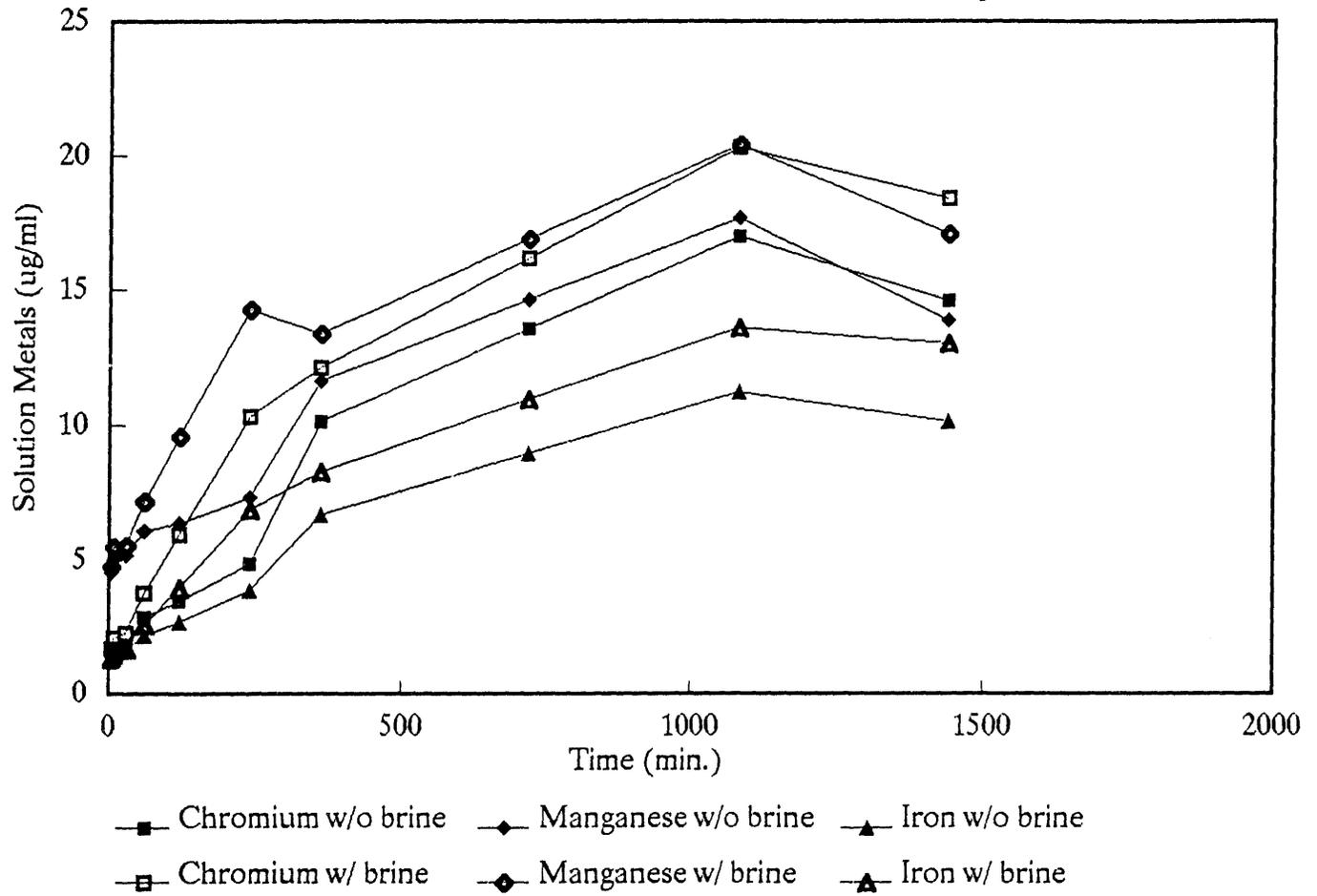
During the carbonate extraction, calcium release peaks in the first 1-2 hours (Figure 3). Net release of the metals chromium, manganese and iron continues almost linearly through four hours, though slower release continues for 18 hours (Figure 4). The counter-ion accelerates the apparent initial rate of metal extraction by 90-100%, but after about 18 hours the net release is only increased by 30-40%. Most of the cesium and cobalt release is virtually immediate, but continues gradually for approximately 18 hours, tracking roughly with the continued metal release (Figure 1). This continuous release probably reflects some nonspecific dissolution beyond the targeted carbonate phase. The counter-ion increases the cesium release by a factor of 5, but the cobalt is increased to about the same extent as the other metals, about 40%. The greater effect for cesium is probably due to its similarity to potassium. No decline in the solution concentrations is apparent for at least 18 hours. This data suggests significant resorption which occur on the same time-scale as the dissolution, such that sites are filled as soon as they are available.

The easily-reducible phase extraction as monitored by the manganese release is essentially complete within five minutes (Figure 5), though iron and calcium continue to be released for at least 24 hours (Figures 5 and 6). The continued release is probably caused by 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 complete in less than an hour. 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

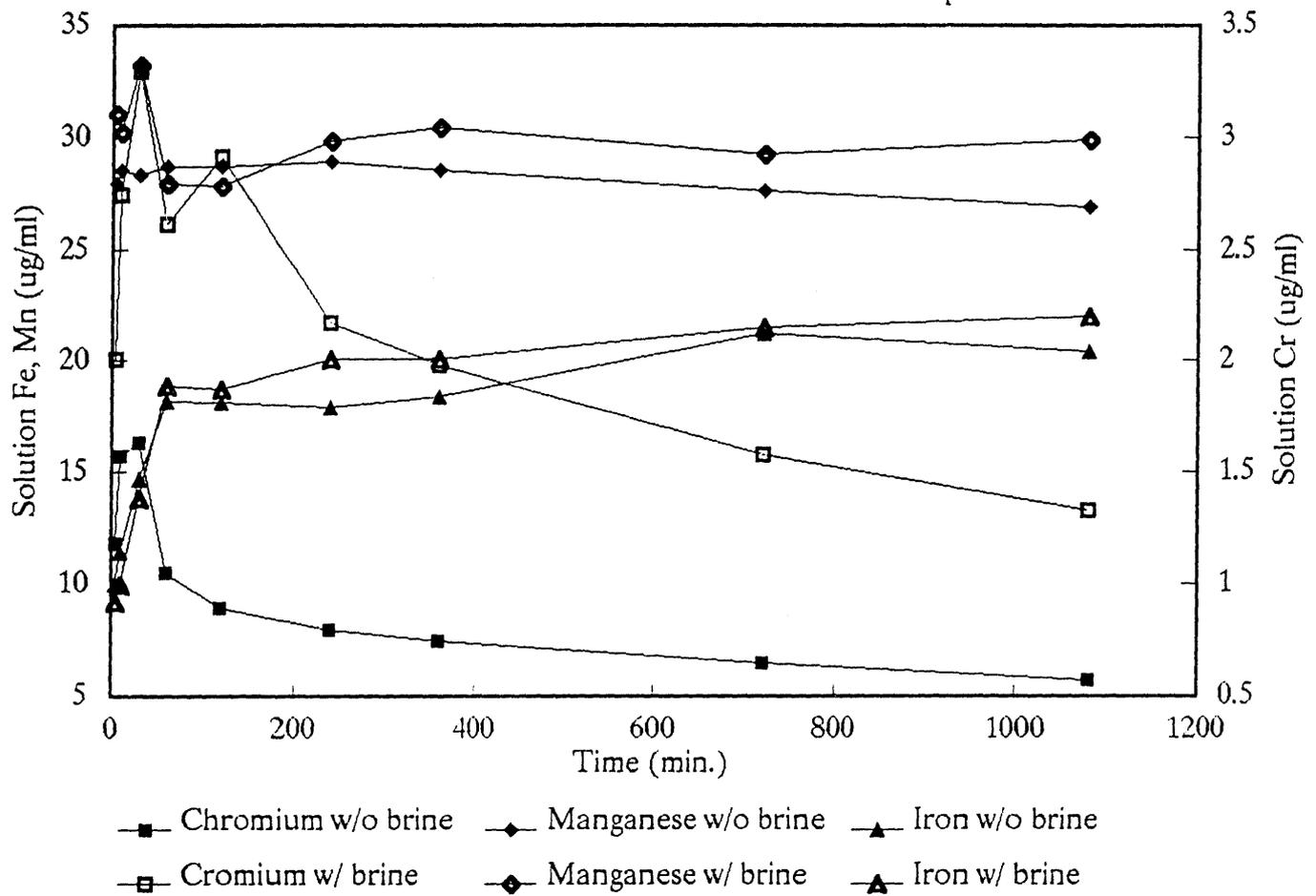
Radionuclide Time Release Profile for Carbonate Extraction
With and Without KNO₃ Brine to Control Resorption



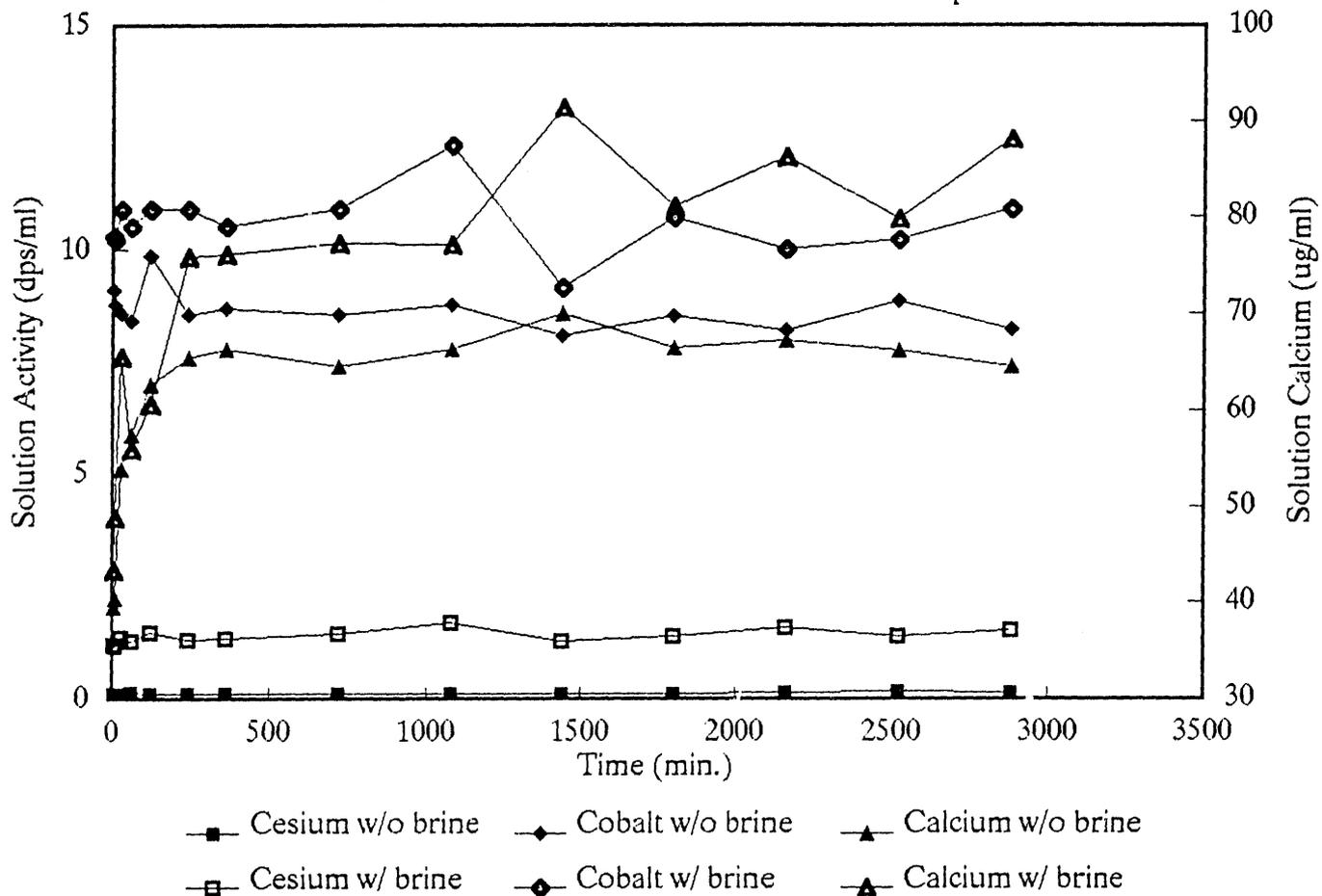
Metals Time Release Profile for Carbonate Extraction
With and Without KNO₃ Brine to Control Resorption



Metals Time Release Profile for Easily-Reducible Phase Extraction
With and Without KNO₃ Brine to Control Resorption



Radionuclide Time Release Profile for Easily-Reducible Phase Extraction
With and Without KNO₃ Brine to Control Resorption



does not markedly affect the loss from solution. None of the other analyte concentrations show a consistent decline over the duration of the experiment. This trend indicates a slower resorption of chromium than 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 7, 8) 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 remaining after the earlier extractions. There is no indication of slow resorption for any of the analytes.

VI. CONCLUSIONS and RECOMMENDATIONS

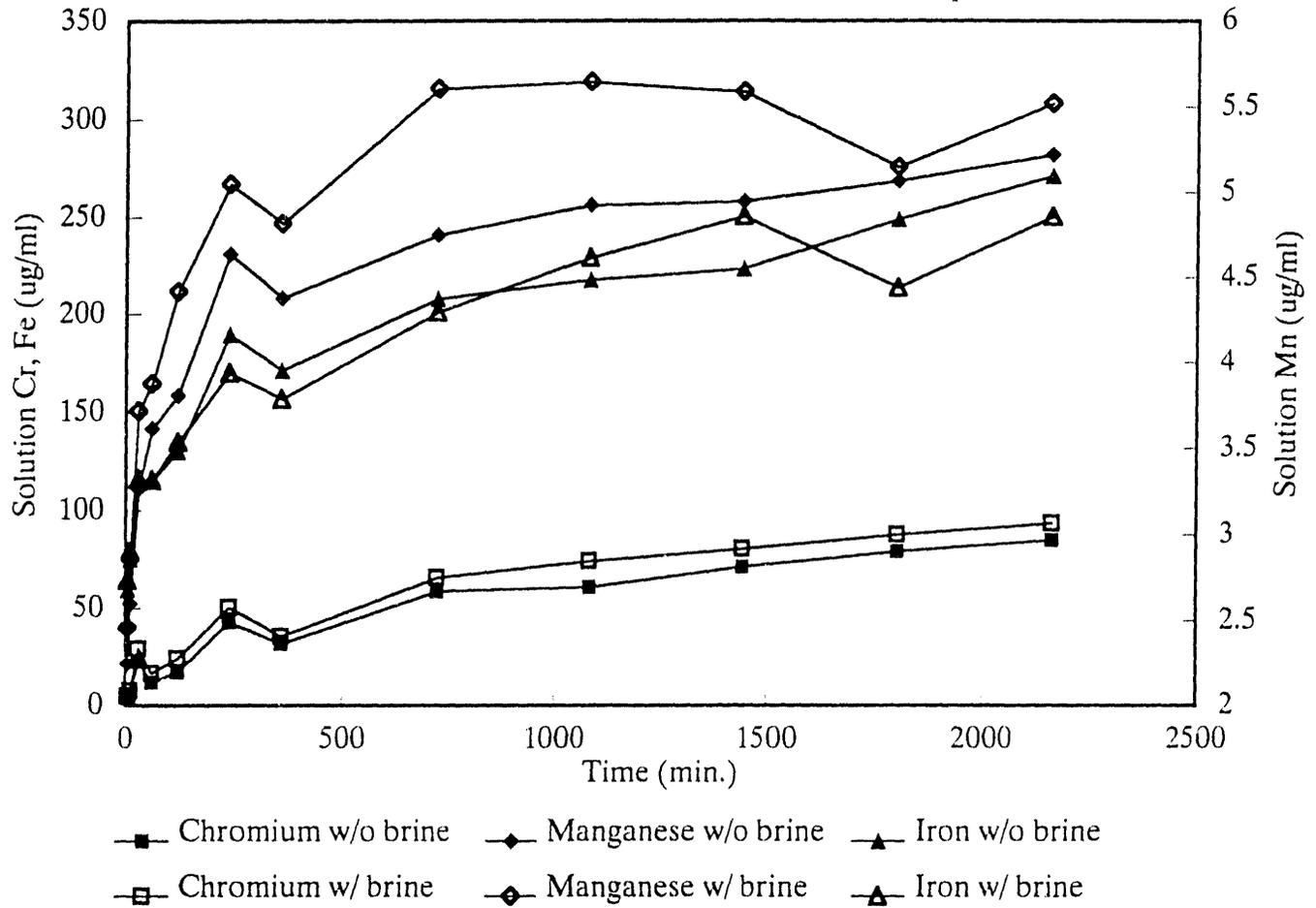
The net release of matrix elements and contaminant species is time dependent, and susceptible to resorption. Sorption may occur as rapidly as dissolution yielding a reduced net dissolution, or more slowly such that contact time becomes critical to prevent recontaminating the substrate. Apparent contaminant distribution may be affected by as much as an order of magnitude for any one phase, causing potentially inappropriate judgement of the results of a treatability study for soil decontamination. The markedly different results for cesium versus cobalt and chromium, the other contaminants of concern, demonstrate the possible selectivity of the counter-ion. Contaminants must be grouped for consideration treatment strategy by chemical similarity rather than regulatory definition.

Though use of counter-ions has potential for mitigating resorption, addition of sorbents such as ion-specific ion exchange media or activated carbon should be explored. These sorbents may not only reduce resorption, but enhance release by maintaining the mass action driver for dissolution of the contaminant out of the substrate.

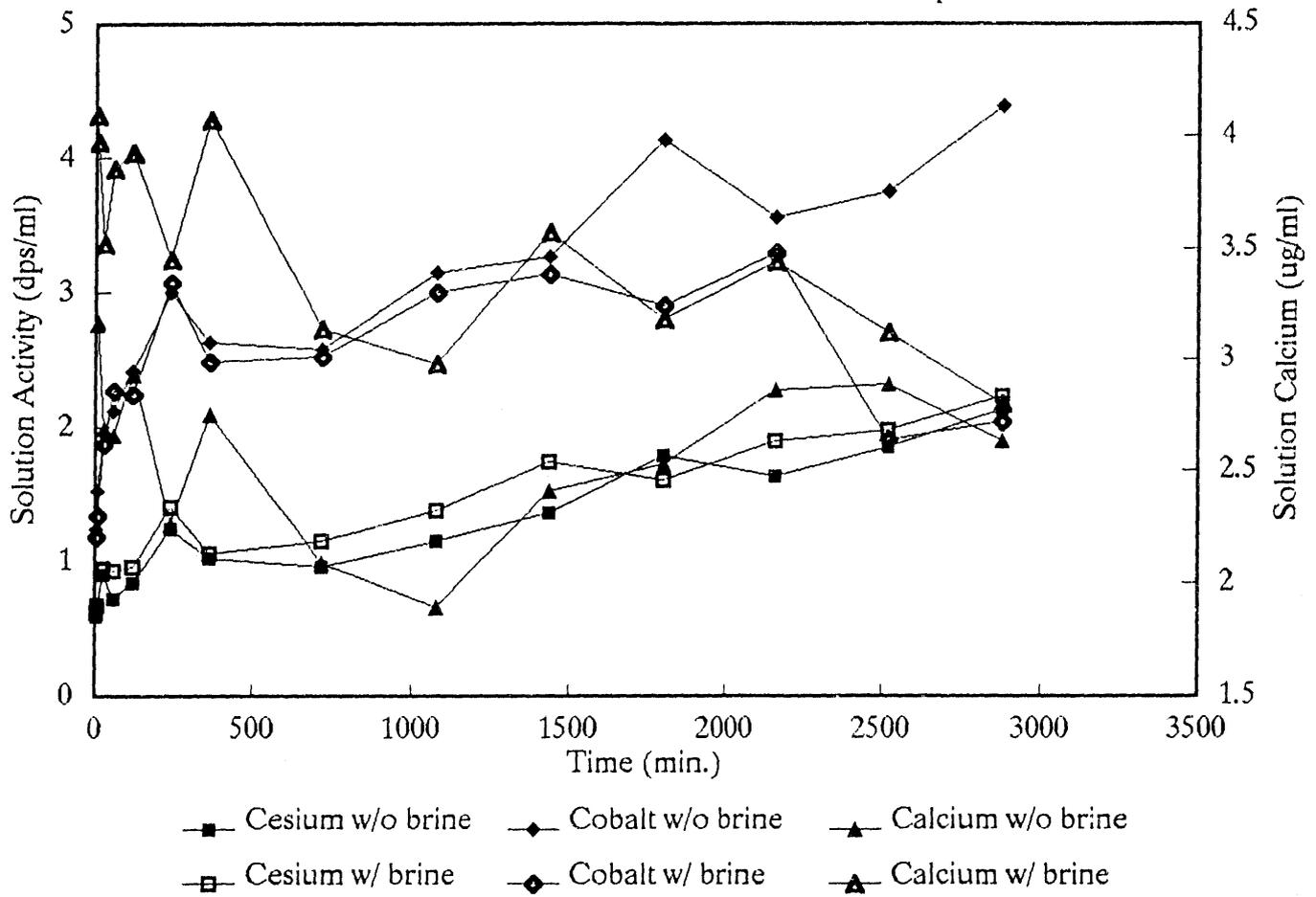
Acknowledgements

The author wishes to credit the analytical chemists at the INEL for providing the technical expertise without which this plan could not have been designed and executed.

Metals Time Release Profile for Moderately-Reducible Phase
With and Without KNO₃ Brine to Control Resorption



Radionuclide Time Release Profile for Moderately-Reducible Phase
With and Without KNO₃ Brine to Control Resorption



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Sequential Extraction Evaluation of Soil Washing for Radioactive Contamination

**Dirk Gombert
Westinghouse Idaho Nuclear Co., Inc.**



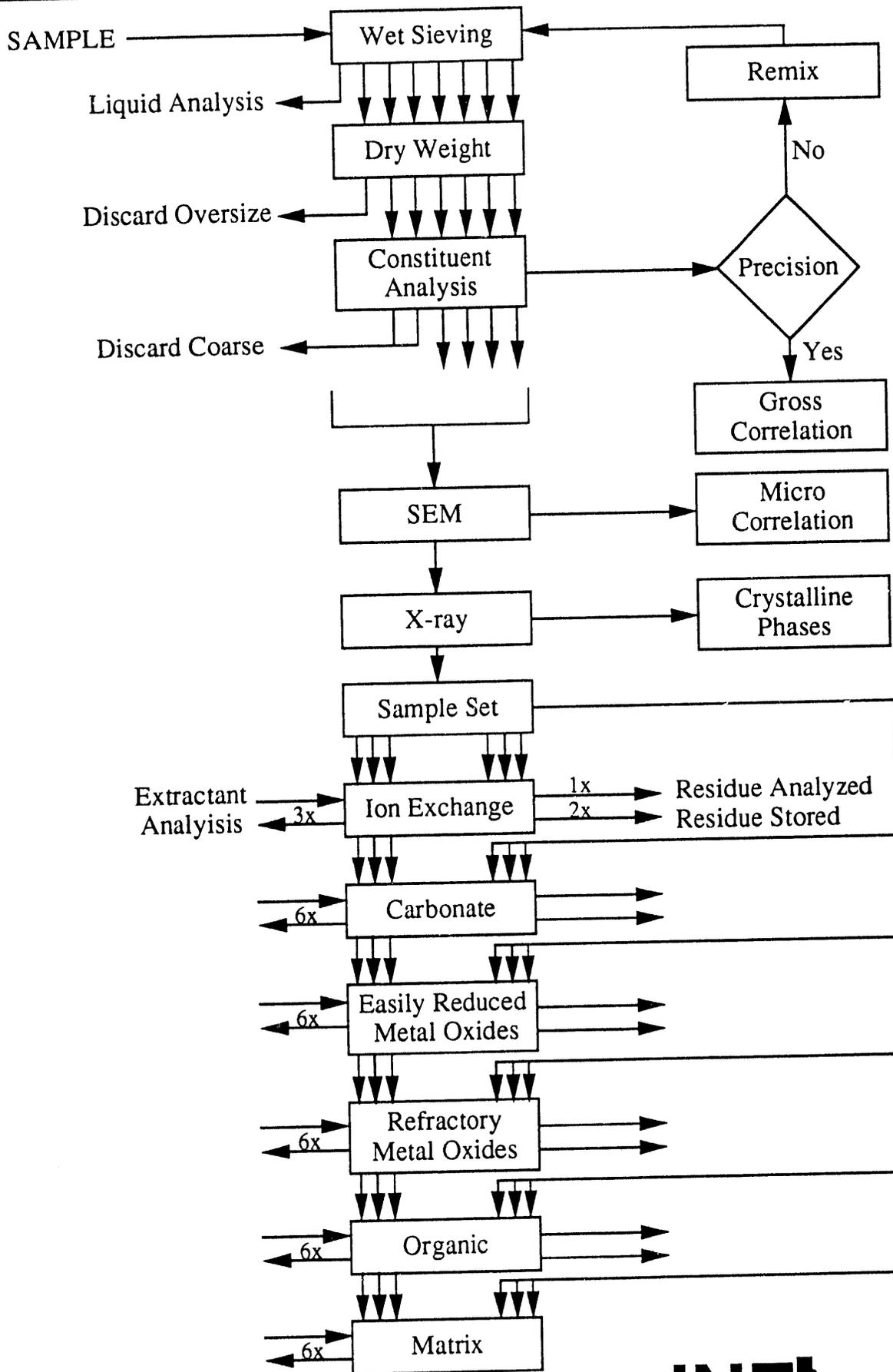
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Sequential Extraction

- Chemically dissect soil
- Progressively more aggressive chemistry
- Determine primary (controlling) mechanism(s)
- Minimize soil dissolution
- Minimize experimentation
- Maximize understanding of problem
 - Focused flowsheet
 - Knowledgeable decision
 - Community acceptance



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Extraction Procedure

Sample: 1 g dry soil (-40 mesh)
Extractant: 20 ml
Monitor: pH, temperature
Conditions: Ambient temperature or 85°C
Continuously shaken

Soil contacted with extractant
Centrifuged
Residue rinsed with deionized water (2x)
Liquid analysis (3x)
Residue Analysis (1x)
Solids stored (2x)
Solids continue to next extraction (3x)



First Extraction

Exchangeable:

Extractant — 1M KNO₃

pH — 7

Temperature — Ambient

Time — 2 Hours

Advantages: K similar size to Cs
 Avoids Ca, Mg precipitation
 Avoids Ca complexing with acetate

Data Analysis: K in extract balance with K in residue
 Cation in extract balance with K loss
 Check for Ca, C-inorg, Fe, Mn, Al, Si



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Second Extraction

Carbonates:

Extractant — 1M NaOAc/HOAc w/wo KNO_3

pH — 5 (monitor ± 0.5)

Temperature — Ambient

Time — Based on time study

Advantages: pH 5 minimizes attack on noncarbonates

Data Analysis: Verify complete removal of inorganic carbon
Check for Fe, Mn, Al, Si



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Third Extraction

Easily reducible metal oxides:

Extractant — 0.1M NH₂OH/HCl, 0.01M HNO₃ w/wo KNO₃

pH — 2 (monitor ± 0.5)

Temperature — Ambient

Time — Based on time study

Advantages: Removes only Mn-oxides and noncrystalline Fe-oxides

Data Analysis: Verify all Mn removed
Check for Al, Si



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Fourth Extraction

Moderately reducible metal oxides:

Extractant — 0.2M NH_4Ox , 0.2M Oxalic acid w/wo KNO_3

pH — 2 (monitor ± 0.5)

Temperature — Ambient

Time — Based on time study

Advantages: Completes removal of hydrated-oxide films without attacking mineral lattice

Data Analysis: Verify surface removal of Fe, Mn
Check for Si



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Fifth Extraction

Organic:

Extractant — 30% H_2O_2 , 0.01M HNO_3 , 3M KNO_3 ,
0.01M HNO_3

pH — 2 (monitor ± 0.5)

Temperature — 85°C

Time — 4 Hours

Advantages: Compromise between complete organic removal and
minimum lattice attack

Data Analysis: Verify C removal
Check for Si



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Sixth Extraction

Lattice:

- Extractant — 1/1 mixture conc HNO_3 /HF
- Temperature — 80°C
- Time — As required to complete digestion

Advantages: HF and HNO_3 compatible with industry
Avoids use of HCl , H_2SO_4

Data Analysis: Provides closure of mass balance, also insight into limiting conditions for soil washing flowsheet



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Data analysis

- Both extractant and residue data
- Removal efficiency
- Mechanism destruction completeness
- Mechanism specificity



Conclusions:

- Objective, defensible evaluation
- Understandable technique
- Provides insight for flowsheet development
or
- Definitive rejection of technology



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