

Leaching of CUB Using a CSTX

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Abstract

Leaching studies of coal utilization byproducts (CUB) are often performed to determine the compatibility of the material in a particular end-use or disposal environment. Typically, these studies are conducted using either a batch or a fixed-bed column technique. The fixed-bed column offers the advantage of a continuous flow of effluent that provides elution profiles with changing elution volume and pH. Unfortunately, clogs can form in fixed-bed leaching columns, either because of cementitious properties of the material itself, such as is seen for FBC fly ash, or because of precipitate formation, such as can occur when a high-calcium ash is subjected to sulfate-containing leachates. A continuous, stirred-tank extractor (CSTX) is being used as an alternative technique that can provide the elution profile of column leaching but without the clogging problems. The CSTX has been successfully employed in the leaching of a flue gas desulfurization produced gypsum that would set-up under traditional column leaching conditions. The results indicate that the leaching behavior depends on a number of factors, including (but not limited to) solubility and neutralization capacity of the mineral phases present, sorption properties of these phases, behavior of the solubilized material in the tank, and the type of species in solution.

Introduction

Over 900 million tons of coal are used annually in the United States, 90% of which is burned for electricity generation (mostly at pulverized coal fired power plants).¹ The burning of coal and the cleaning of flue gases produces a large volume of material or residue, collectively referred to as coal utilization byproducts (CUB). CUBs include fly ash, bottom ash, boiler slag, fluidized bed combustion (FBC) ash and flue gas desulfurization (FGD) material. It is estimated that over 70 million tons of fly ash and 29 million tons of FGD material were generated in 2003.² FGD units typically use a lime or limestone reagent to capture SO₂ gas, much of which is subsequently converted to gypsum (CaSO₄•2H₂O). FGD produced gypsum is mainly used as a substitute for natural gypsum in the manufacturing of wallboard, though it is also be used, to a lesser extent, as a soil amendment or as an additive in cement. Coal contains a number of trace metals, and as a result CUBs typically contain low concentrations of these metals. As stricter emission control/reduction policies, particularly those focusing on mercury, are implemented, an increase in metals concentration in these byproducts will likely occur, along with a transfer of the environmental burden.¹

In general, leaching techniques focus on the potential release of heavy metals to the surface and groundwater environments. Leaching studies of CUBs are often performed to determine the compatibility of the material in a particular end-use or disposal environment.^{3,4,5} Typically, these studies involve either a batch or a fixed-bed column technique.^{6,7,8} Batch leaching techniques only provide information on metals release at a set pH, not over a range. The fixed-bed column offers the advantage of a continuous flow of effluent that provides elution profiles with changing elution volume and pH. However, clogs can form in fixed-bed leaching columns, either because of cementitious properties of the material itself, such as is seen for FBC ash, or because of precipitate formation, such as can occur when a high-calcium ash is subjected to sulfate-containing leachates. Material that is too fine grained, such as FGD gypsum, also causes permeability problems. A continuous, stirred-tank extractor (CSTX) is an alternative technique that can provide the elution profile of column leaching but without the clogging problems. Unlike fixed-bed column and batch leaching techniques, a CSTX allows fundamental chemical information to be obtained, including reaction rates, equilibrium constants, effective solubility products, and the effect of pH changes. Fundamental data can then be used in geochemical models to predict results in a given environment.

One notable disadvantage of a CSTX is that extraction data do not reflect an actual, end use environment, as there is no environment where continual mixing occurs. Solubilized material is not at once removed from the reactor as it is with column leaching. Instead, it is sequentially diluted by incoming leachant over time presenting the possibility for interactions between the solubilized material and solids remaining in the tank.

Materials and Methods

The apparatus (Figure 1) consisted of a 6-liter, all-glass and Teflon reactor (Ace Glass 6386-28) with a mechanical paddle stirrer and a bottom-outlet filter (porosity D) reinforced with a 0.45 μm membrane filter. Oxidation-reduction potential (ORP) and pH were monitored using a Mettler Toledo SevenMulti unit monitored by a computer. Care was taken to seal the apparatus from the laboratory atmosphere by appropriate joint seals and a continuous nitrogen gas flush. Influent and effluent flow rates were controlled using FMI model RSHY pumps. The effluent flow traveled through an in-line filter and was collected in a nitrogen gas purged receptacle until an ISCO model 3700 Automatic Liquid Sampler (ALS) collected it at set intervals. All aqueous samples were analyzed for major and trace elemental composition (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Sr, Zn) using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Hg concentrations were determined using Cold Vapor Atomic Adsorption (CVAA).

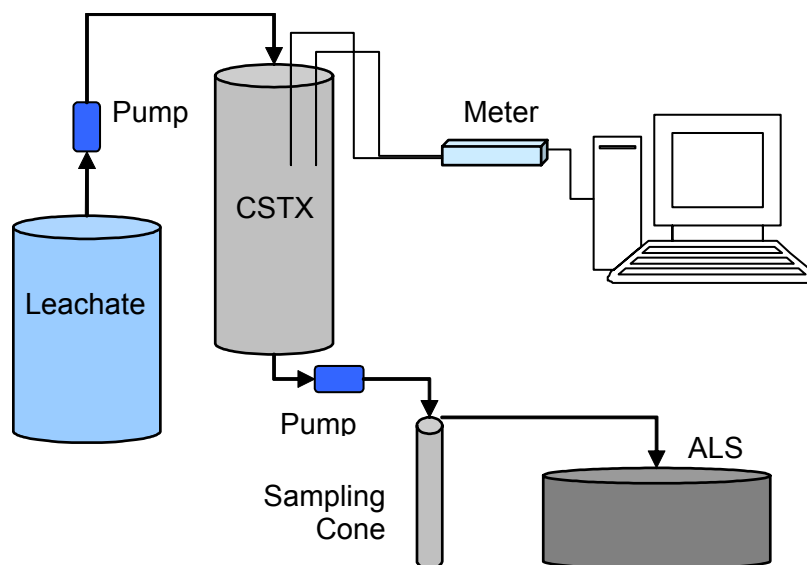


Figure 1. CSTX schematic

FGD gypsum was investigated in this study. Total metal concentrations in the solid were determined using microwave assisted digestion with aqua regia and hydrofluoric acid followed by dilution and analysis using ICP-OES. Mercury concentration in the solid was determined using a Milestone DMA-80.

Approximately 200 g of gypsum was placed in the tank with 4L of Milli-Q[®] water (MQW, 18M Ω •cm). The tank was subjected to a nitrogen purge throughout the experiment. An initial MQW rinse was employed until the pH in the tank stabilized. After this rinse, the material underwent an initial acid leach using 0.00023 N HCl, followed by a subsequent acid leach using 0.0023 N HCl. The extraction continued until the pH < 3. A total of 211 samples were collected. The remaining material in the tank was removed and filtered. The solid residue (<1 g) was dried in a desiccator and analyzed using microwave assisted digestion followed by dilution and analysis using ICP-OES. Mercury concentration was determined using DMA-80.

Results and Discussion

The total amount of each element extracted, the amount present in the original solids, and percent extracted are presented in Table 1, and material balances for the individual elements are presented in Table 2. The material balances for Ca and S are close to 100%, indicating essentially complete recovery of the gypsum. Material balances could not be determined for As, Be, Cd, Co, Mo, Ni, Pb and Se, because these metals are below the detection limit in the solid gypsum material, although their presence in either the residue or the leachate, or both, indicate levels in the solids are likely near the detection limits, as opposed to simply not being present. Certain metals (including Al, As, Co, Cr, Fe, Mo, Ni and Pb) report more to the residue than to the extract. It is important to note that Hg reported entirely to the residue, giving a material balance of 102%.

| | Extracted Totals (ug) | Extracted Amount per gram in Tank (ug/g) | Amount in Solid (ug/g) | Amount Extracted (%) |
|----|-----------------------|--|------------------------|----------------------|
| Ag | 88 | 0.58 | 5 | 12 |
| Al | 7676 | 50 | 192 | 26 |
| As | 0 | 0 | < 1 | -- |
| Ba | 2022 | 13 | 33 | 40 |
| Be | 5 | 0.04 | < 0.1 | -- |
| Ca | 42602944 | 278596 | 290000 | 96 |
| Cd | 9 | 0.06 | < 2 | -- |
| Co | 0 | 0 | < 2 | -- |
| Cr | 106 | 0.69 | 3 | 24 |
| Cu | 236 | 1.54 | 8 | 19 |
| Fe | 17819 | 117 | 367 | 32 |
| Hg | 0 | 0 | 0.14 | 0 |
| K | 156501 | 1023 | 741 | 138 |
| Mg | 306832 | 2006 | 2146 | 93 |
| Mn | 739 | 4.83 | 6 | 82 |
| Mo | 7 | 0.05 | < 3 | -- |
| Na | 93795 | 613 | 32000 | 2 |
| Ni | 5 | 0.03 | < 3 | -- |
| P | 5014 | 33 | 66 | 49 |
| Pb | 0 | 0 | < 6 | -- |
| S | 34784234 | 227467 | 212030 | 107 |
| Se | 1064 | 7 | < 8 | 87 |
| Sr | 44727 | 292 | 313 | 94 |
| Zn | 1536 | 10 | 18.3 | 55 |

Table 1. Extraction results for a FGD gypsum leached in a CSTX

By examining patterns of metals release, it is possible to identify and interpret different processes occurring in the CSTX. For the FGD gypsum, a number of patterns indicating different processes are evident, including: solubility driven release, a neutralization reaction driven release, release followed by adsorption, and no release. A few complex behaviors not explained by a single process are also evident.

Some metals, including As, Co, Hg and Pb exhibit no release. These metals were measurable in the residue, but not in the original gypsum (except Hg) added to the tank, nor in the extracted samples, indicating they are likely present in quantities close to the detection limit (see Table 1) and are concentrated in the residue. This behavior could result from either an initially strong sorption of release followed by immediate sorption onto solid material remaining in the tank.

Solubility driven release is exhibited by Ca and S (Figure 2), as well as Se and Sr (not shown). As seen in Figure 2, the concentrations of Ca and S first seen at the beginning of the extraction remain relatively constant throughout the experiment, indicating

continuous dissolution at near equilibrium conditions. Dissolution of the CaSO_4 is controlled by its solubility product (K_{sp}) and therefore by the volume of liquid going through the system; it does not necessarily depend on a change in pH. It is informative to compare the experimental molar concentrations for Ca and S to predicted molar concentrations based on the K_{sp} . Using the literature value of 2.51×10^{-5} for the K_{sp} of gypsum at 25°C , a predicted molar concentration for Ca and S can be determined.⁹

| | Amount in residue (ug) | Extracted Totals (ug) | Residue + Extracted (ug) | Initial Amount added to CSTX (ug) | Balance (%) |
|----|------------------------|-----------------------|--------------------------|-----------------------------------|-------------|
| Ag | < 0.67 | 88 | 88 | 758 | 12 |
| Al | 20684 | 7676 | 28361 | 29331 | 97 |
| As | 11 | 0 | 11 | < 1223 | -- |
| Ba | 2095 | 2022 | 4117 | 4998 | 82 |
| Be | 0.56 | 5 | 6 | < 15 | -- |
| Ca | 2062 | 42602944 | 42605006 | 44346800 | 96 |
| Cd | 4 | 9 | 12 | < 306 | -- |
| Co | 6 | 0 | 6 | < 306 | -- |
| Cr | 149 | 106 | 255 | 439 | 58 |
| Cu | 22 | 236 | 259 | 1237 | 21 |
| Fe | 19078 | 17819 | 36897 | 56168 | 66 |
| Hg | 22 | 0 | 22 | 22 | 102 |
| K | 7363 | 156501 | 163864 | 113389 | 145 |
| Mg | 4739 | 306832 | 311572 | 328227 | 95 |
| Mn | 79 | 739 | 818 | 898 | 91 |
| Mo | 14 | 7 | 21 | < 459 | -- |
| Na | 1433 | 93795 | 95228 | 4893440 | 2 |
| Ni | 22 | 5 | 27 | < 459 | -- |
| P | 897 | 5014 | 5911 | 10156 | 58 |
| Pb | 20 | 0 | 20 | < 765 | 3 |
| S | 6962 | 34784234 | 34791196 | 32423628 | 107 |
| Se | 37 | 1064 | 1100 | < 1217 | -- |
| Sr | 64 | 44727 | 44791 | 47788 | 94 |
| Zn | 396 | 1536 | 1933 | 2793 | 69 |

Table 2. Material balance from the continuous leaching of a FGD gypsum in a CSTX

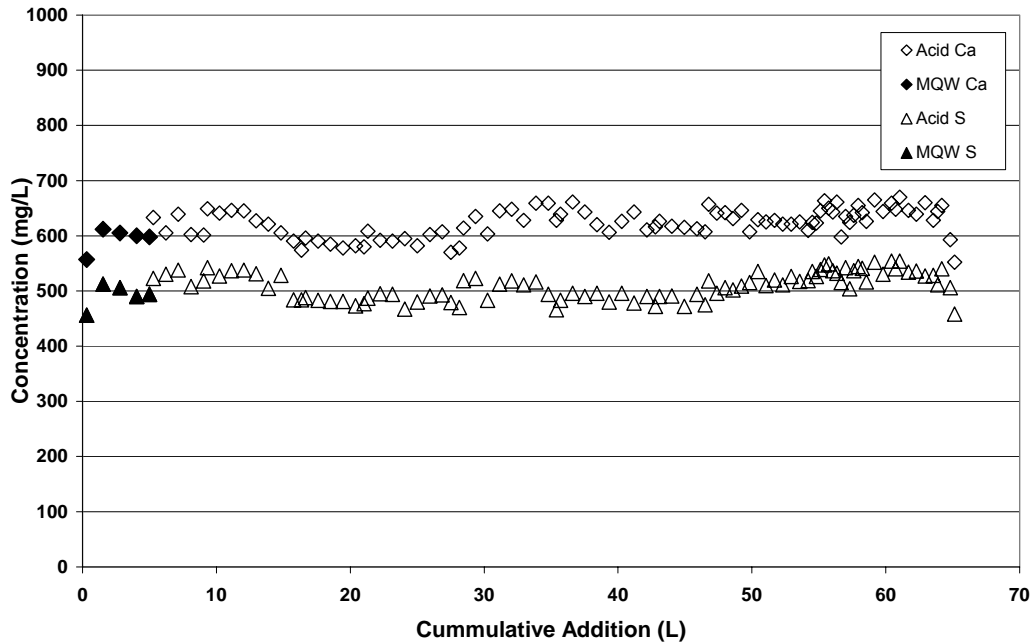


Figure 2. Concentration of Ca and S with cumulative addition of leachate.

The dissolution of gypsum is described by the following reaction (waters of hydration are not considered):



Defining x as the number of moles per liter of CaSO_4 that dissolve implies that a saturated solution would contain x mol/L of Ca^{2+} and x mol/L of SO_4^{2-} :

$$K_{sp} = 2.51 \times 10^{-5} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = x^2 \quad (2)$$

$$X = 5.01 \times 10^{-3} \text{ mol/L} \quad (3)$$

Thus, the ideal molar solubility of CaSO_4 in water at 25°C is expected to be 5.01×10^{-3} mol/L. The experimental concentration of Ca (600 mg/L) gives 15×10^{-3} mol/L. This indicates the liquid in the tank is supersaturated compared to ideal behavior.

A number of elution profiles were obtained in which a more or less rapid rise in concentration was followed by an initially rapid but progressively slower decrease in concentration. These are considered individually and in more detail in the discussion of Figures 3 – 5. In each of these cases, the post-maximum decrease is compared to that expected from a simple washing of the material out of the CSTX by the continuing flow of the fresh leachate. This “predicted” decrease was calculated using the inlet and outlet pump flow rates to determine the extent of dilution for each successive sample. The validity of the calculations was established in separate experiments not shown here

in which a soluble tracer was added in a single portion to the CSTX and its removal monitored.

Figure 3 presents the actual (triangles) and predicted (solid line) concentrations obtained for Mg. Mg elution begins with the addition of the stronger acid, gradually increases to a maximum then decreases in conjunction with the drop in pH. Such behavior is indicative of the acid neutralizing capacity of the material; Mg may be present as a carbonate that acts to buffer the system. The pH in the CSTX does not drop until this material is completely consumed. The post neutralization behavior is well-modeled by the successive dilution calculations. The solubilized Mg is not removed from the tank instantaneously; it washes out over time, producing the tail on the curve. Magnesium exhibits a neutralization reaction driven release.

The elution pattern for Cd (Figure 4) shows a spike in concentration followed by a sudden decrease. This post-release behavior is not consistent with that of most of the other metals, nor with the predicted sequential dilution behavior. Its disappearance from solution is much faster than expected, indicating a release followed by rapid adsorption onto another phase in the tank. The solid line in Figure 4 represents the predicted behavior of Cd, though the detection limit of Cd is 0.5 ppb, so the values < 0.5 ppb on the graph would not be evident. It is unlikely that readsorption behavior such as this would be seen in the typical batch or fixed-column leaching tests. Cd exhibits leaching behavior controlled by readsorption processes.

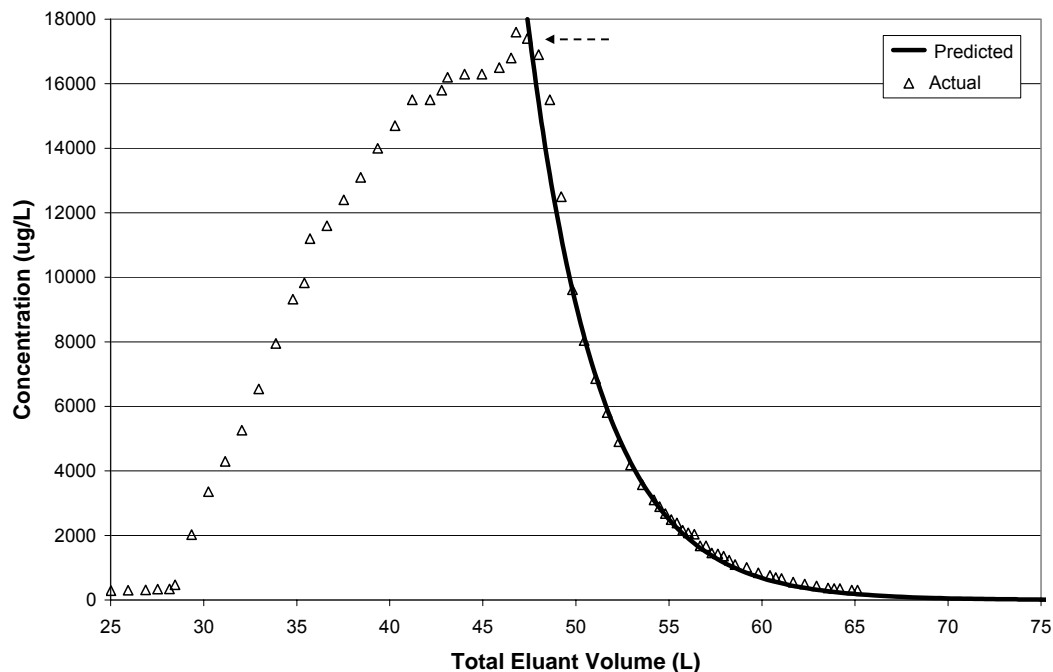


Figure 3. Concentration of Mg (predicted and actual) with cumulative addition of leachate. Dashed arrow represents point at which pH begins to drop.

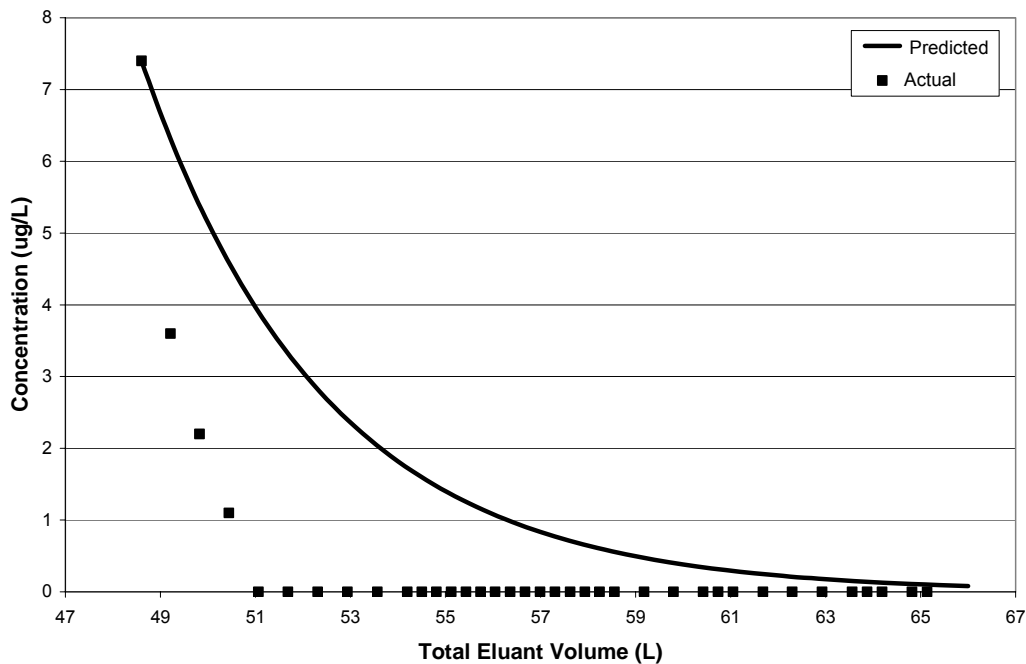


Figure 4. Concentration of Cd with cumulative addition of leachate.

Aluminum and Fe exhibit behaviors too complex to be explained by any one simple mechanism. The aluminum concentration initially spikes (Figure 5) and then decreases too slowly to be accounted to an instantaneous release followed by a sequential dilution by the leachant. A shrinking core model might be used to explain this pattern. Such a model would assume that the rate of dissolution per unit of surface area of each particle in the tank was equal. As the material decreases in size, a corresponding decrease in surface area (and surface reaction sites) would occur, resulting in a lower rate of dissolution for Al.

Fe shows an even more complex behavior in which it increases in concentration in at least two steps until it reaches a maximum, followed by a pronounced decrease, but not to zero (Figure 6). The behavior is characteristic of neither an instantaneous release nor a smooth neutralization release followed by dilution. This especially complex behavior may indicate the presence of several Fe phases (or even an Fe and Al phase), some of which may be dissolving at different rates. The shrinking core model may also apply to these phases. Further investigations are in progress to determine the specific processes controlling Fe and Al behavior.

The post-leaching residue accounted for less than 1% of the original material, with only traces of remaining gypsum, but higher concentrations of Fe and Al, as well as As, Co, Hg and Pb (discussed earlier). It appears that the phase responsible for retention of the As, Co, Hg and Pb is not the fine, high-surface-area calcium sulfate, but more likely an iron or mixed iron and aluminum phase. Due to an insufficient amount of residue, mineralogy could not be determined.

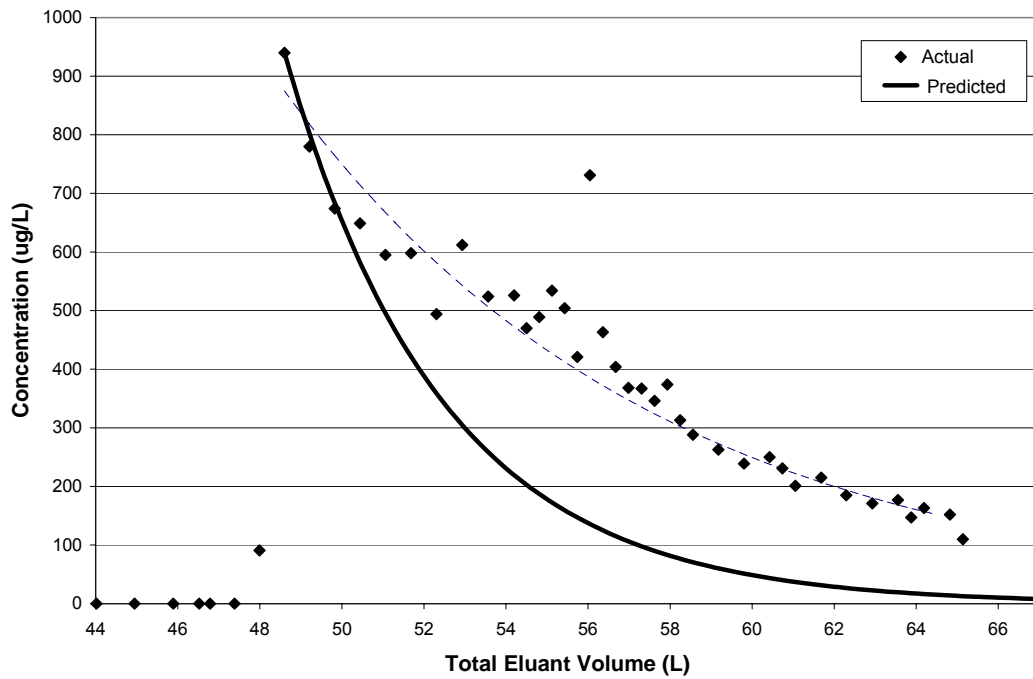


Figure 5. Concentration of Al with cumulative leachate addition

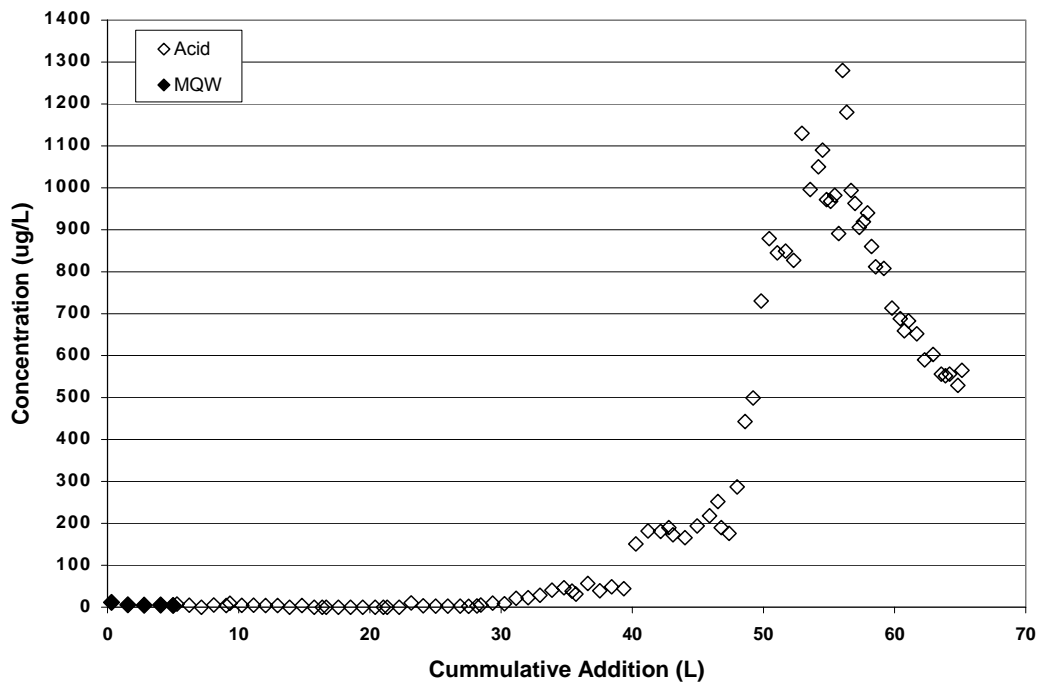


Figure 6. Concentration of Fe with cumulative leachate addition.

Conclusion

The use of a CSTX allows the chemistry of the leaching process to be studied at a level unachievable through more traditional batch and column techniques. The elemental behavior of individual elements depends on a number of factors, including (but not limited to) solubility of the mineral phases present, sorption properties of these phases, behavior of the solubilized material in the tank, the type of species in solution and the neutralization capacity of the minerals.

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