

Leaching of FGD Byproducts 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. Fixed-bed columns offer 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 fluidized bed combustion (FBC) fly ash, or because of precipitate formation, such as can occur when a high-calcium ash is subjected to sulfate-containing leachates. Also, very fine-grained materials, such as gypsum, do not provide sufficient permeability for study in a fixed-bed column. 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 low permeability problems. The CSTX has been successfully employed in the leaching of flue gas desulfurization products that would not be sufficiently permeable 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. In addition, leaching to near-exhaustion of a wallboard produced from FGD gypsum has allowed the isolation of a highly adsorptive phase. This phase appears to be present in at least some FGD gypsums and accounts for the immobilization of trace metals such as arsenic, cobalt, lead, and mercury.

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). CUB 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 as calcium sulfite, most of which is subsequently converted to gypsum (CaSO₄ · 2H₂O) in forced oxidation units. FGD produced gypsum is mainly used as a substitute for natural gypsum in the manufacturing of wallboard, though it can 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 CUB 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.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 quickly provide information on metals release at a set pH, rather than 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 permeability 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, as well as 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 removed from the reactor as it is with column leaching; it is sequentially diluted by incoming leachant over time. The possibility exists for interactions between the solubilized material and remaining solids 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 data were collected using a Mettler Toledo SevenMulti unit interfaced to a computer. Care was taken to seal the apparatus from the laboratory atmosphere by appropriate joint seals and a continuous nitrogen gas flush. In addition, the two ports containing the pH and ORP leads were sealed with wax. Influent and effluent flow rates were controlled using FMI model RHSY pumps. The effluent flow traveled through an in-line, 0.45 micron filter and was accumulated in a nitrogen-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, Ti Zn) using Inductively

Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Hg concentrations were determined using Cold Vapor Atomic Adsorption (CVAA).

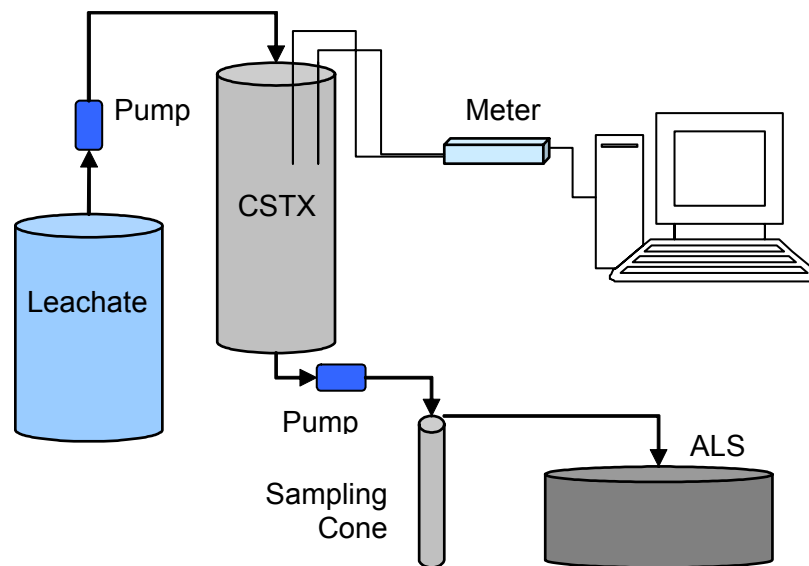


Figure 1. CSTX schematic

A wallboard manufactured from FGD gypsum was investigated in this study. The paper from the wallboard was removed and the sample was ground to a fine powder using a Brinkman Centrifugal Grinding Mill. Approximately 200 g of the wallboard was placed in the tank with 4L of Milli-Q[®] water (MQW, 18M Ω ·cm). The tank was subjected to a nitrogen purge to maintain an anoxic environment 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 240, 300-mL samples were collected. The remaining material in the tank was removed and filtered. The solid residue (< 3 g) was dried in a desiccator and elemental concentrations determined using the two methods described below. X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert Pro MPD and morphology was determined using an Aspek PSEM 2000 with EDS.

Total metal concentrations in the solid were determined using two methods. In the first method, the solid was treated with 20 mL aqua regia, heated to dryness, re-dissolved in 50 mL warm 10% nitric acid, filtered and analyzed using ICP-OES. In the second method, the solid was digested in 10:1 excess of molten lithium *meta*-borate for 20 minutes, taken up in warm 7% hydrochloric acid and analyzed using ICP-OES. Mercury concentration in the solid was determined using a Milestone 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 elemental data for the residue and the 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 wallboard gypsum. Material balances could not be determined in the case of Ag, As, Be and Pb, because these metals were below the detection limit in the original wallboard 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, Ba, Cr, Fe, Ni, Si, and Ti) partition more to the residue than to the extract. It is possible that Co, Mo and some of the other elements with low balances leached out at levels below detection over the course of the experiment. Mercury reported entirely to the residue, giving a material balance of 109%.

Element	Amount in Wallboard* (ug/g)	Total Leached (ug)	Amount Leached per gram of Wallboard (ug/g)	Percent Leached (%)
Ag	< 0.25	0	0	--
Al	689	13000	96.8	14
As	< 2	0	0	--
Ba	33.5	1320	9.80	29
Be	< 0.1	1.44	0.01	--
Ca	297000	40300000	300000	101
Cd	0.97	16.0	0.12	12
Co	0.67	0	0	0
Cr	3.56	45.4	0.34	9
Cu	21.3	200	1.49	7
Fe	468	13000	96.8	21
Hg	0.15	0.15	0.001	1
K	1430	97300	724	51
Mg	2740	419000	3120	114
Mn	8.47	1020	7.56	89
Mo	8.14	0	0	0
Na	726	139000	1035	142
Ni	5.99	15.7	0.12	2
P	152	5950	44.30	29
Pb	< 1	0	0	--
S	275000	33400000	249000	91
Se	6.40	1020	7.62	119
Si	9070	22500	168	2
Sr	335	43400	323	96
Ti	81.9	0	0	0
Zn	39.0	1300	9.66	25

Table 1. Extraction results for wallboard leached in a CSTX

Element	Initial amount added to CSTX (ug)	Amount in residue (ug)	Total Leached (ug)	Residue + Leached (ug)	Balance (%)
Ag	< 33.6	< 1	0	0	--
Al	92500	59100	13000	72100	78
As	< 268.6	28.8	0	28.8	--
Ba	6158	2750	1320	4070	66
Be	< 13.4	< 0.1	1.44	1.44	--
Ca	39800000	33300	40300000	40333300	101
Cd	131	6.34	16.0	22.3	17
Co	90.1	12.7	0	12.7	14
Cr	478	319	45.4	365	76
Cu	2860	364	200	564	20
Fe	62900	41200	13000	54200	86
Hg	19.8	21.4	0.15	21.6	109
K	193000	15600	97300	112900	59
Mg	368000	16400	419000	435400	118
Mn	1140	157	1020	1177	103
Mo	860	29.8	0	29.8	3
Na	97600	3620	139000	142620	146
Ni	804	90.0	15.7	106	13
P	20500	2770	5950	8720	43
Pb	< 134.3	44.6	0	44.6	--
S	37000000	13800	33400000	33413800	90
Se	860	82.9	1020	1103	128
Si	1220000	884000	22500	906500	74
Sr	45100	195	43400	43595	97
Ti	11000	4300	0	4300	39
Zn	5240	884	1300	2184	42

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

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

Some metals, including As, Hg, and Pb exhibit no release. These metals were all measurable in the residue, but As and Pb were not measurable in the original wallboard added to the tank, nor in the leachates, indicating they are likely present in the wallboard in quantities close to the detection limit (see Table 1) and become concentrated in the residue. Because these elements were not present in any of the leachate samples, if release (at concentrations below detection limit) followed by sorption onto the solid material remaining in the tank occurred, the rate of re-sorption was much faster than the rate of release.

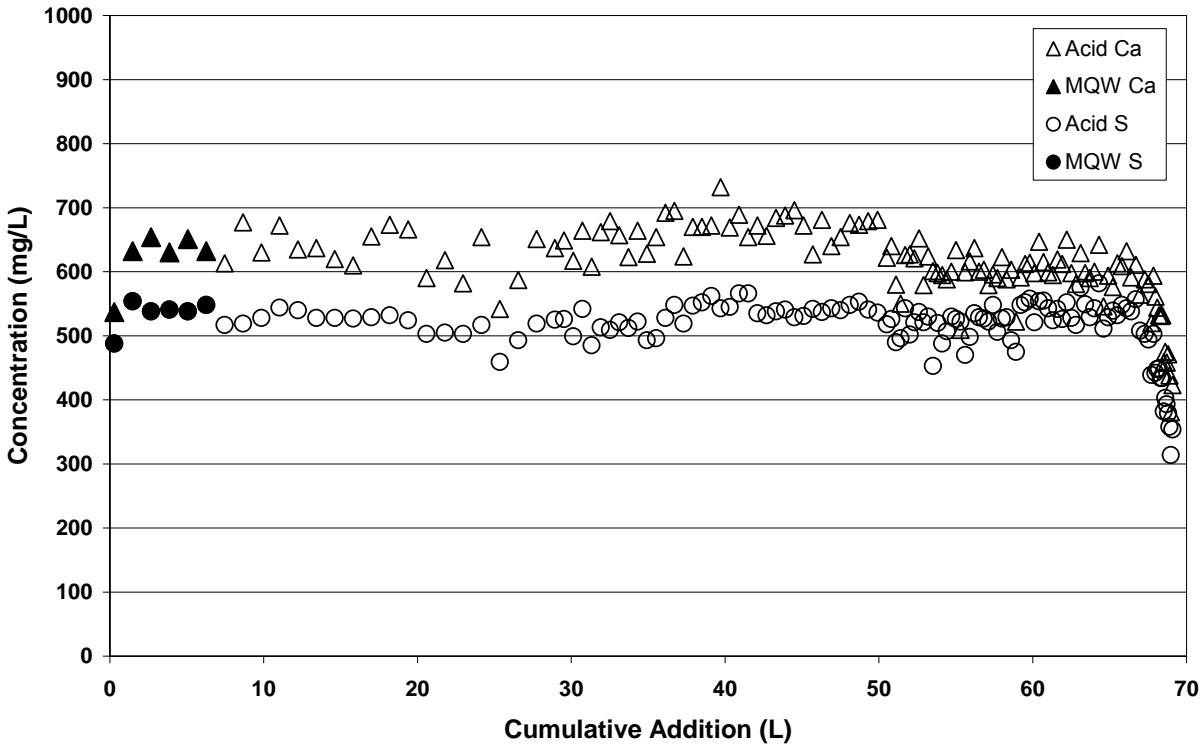


Figure 2. Concentration of Ca and S with cumulative addition of leachate.

Solubility driven release is exhibited by Ca and S (Figure 2), as well as Sr (not shown). As seen in Figure 2, the concentrations of Ca and S seen at the beginning of the extraction remain relatively constant throughout the experiment, indicating continuous dissolution at steady state conditions. At flow rates sufficiently slow compared to dissolution rates, steady state concentrations approach equilibrium values. Under these conditions, dissolution of CaSO_4 is controlled by its solubility product (K_{sp}) and does not necessarily depend on the 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

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. In contrast, the concentration of Ca (625 mg/L) converts to 15.6×10^{-3} mol/L, about 3 times higher than predicted. The difference between the predicted and actual values indicates that the liquid in the tank is supersaturated compared to ideal behavior. It is possible that the material used in this study is amorphous and would therefore have a much higher solubility than crystalline CaSO_4 due to less crystal lattice energy stabilization. Additionally, finely divided molecular CaSO_4 may have passed through the $0.45 \mu\text{m}$ filters and could account for the difference in K_{sp} , rather than a large excess (relative to K_{sp}) of ions.

Several 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 and 4. 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 tapers off 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.

Aluminum and Fe exhibit behaviors too complex to be explained by any one simple mechanism. The Al concentration initially spikes (Figure 4) and then decreases following the expected pattern of sequential dilution by the incoming leachant. However, the Al concentration does not taper off and produce a tail on the curve as would be expected. Instead, the concentration begins to increase again, indicating bimodal dissolution and the possible presence of two separate aluminum phases.

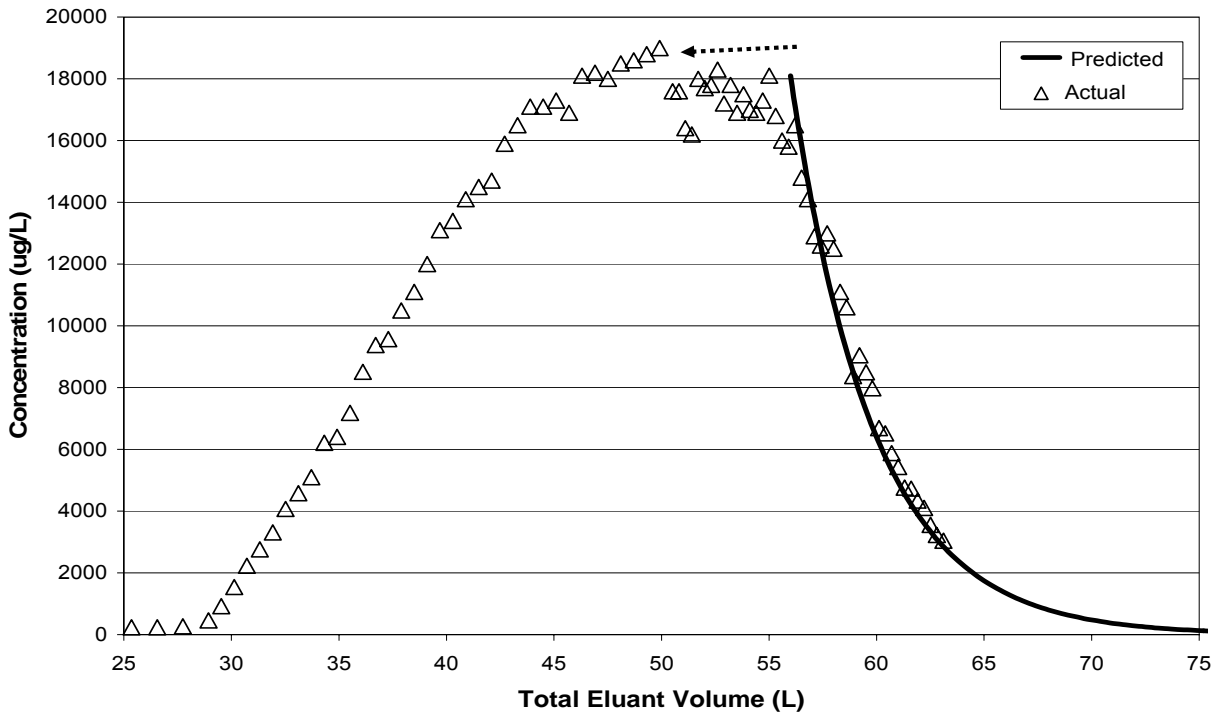


Figure 3. Concentration of Mg with cumulative addition of leachate. Line represents expected post-release concentration based on the inlet and outlet flows. Dashed arrow represents point at which pH begins to rapidly drop.

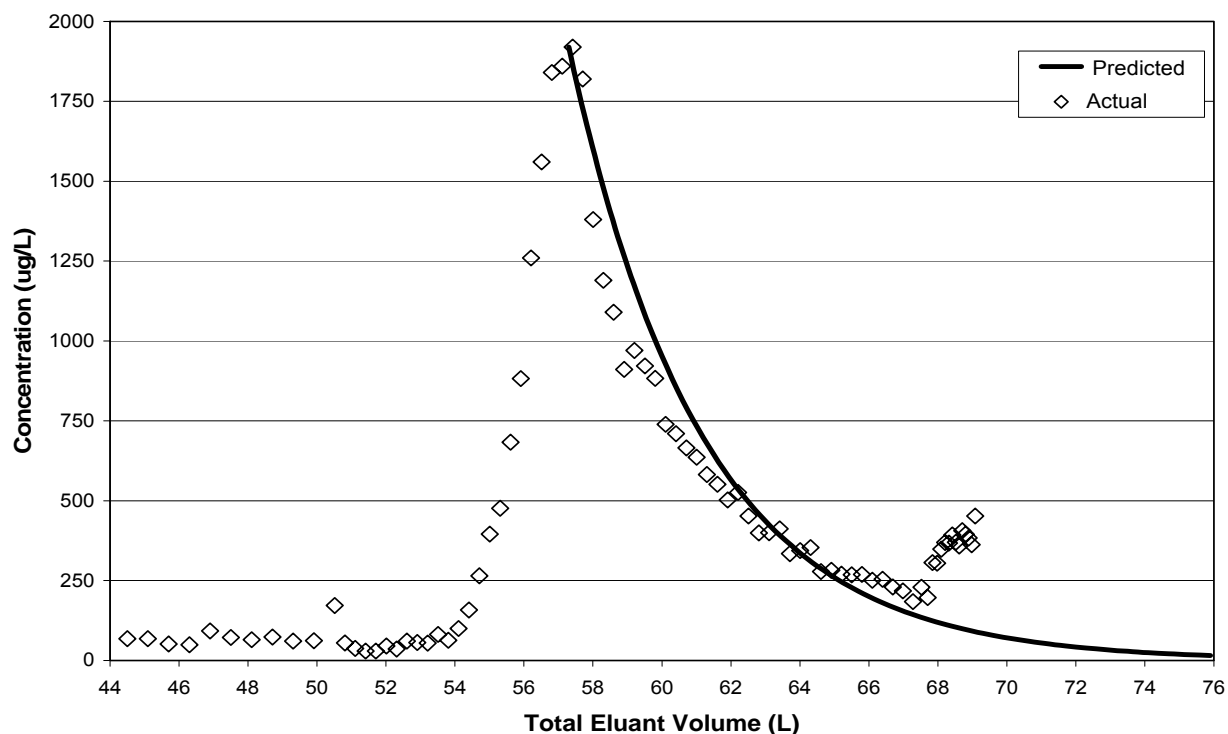


Figure 4. Concentration of Al with cumulative leachate addition. Line represents expected post-release concentration based on the inlet and outlet flows.

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 short, pronounced decrease, only to increase again (Figure 5). 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 Fe and Al phases, which dissolving at different pH values and/or rates. As seen in Figure 6, the release of Fe and Al increase significantly only after the buffering capacity of the Mg compound is exhausted. Further investigations are in progress to determine the specific processes controlling Fe and Al behavior.

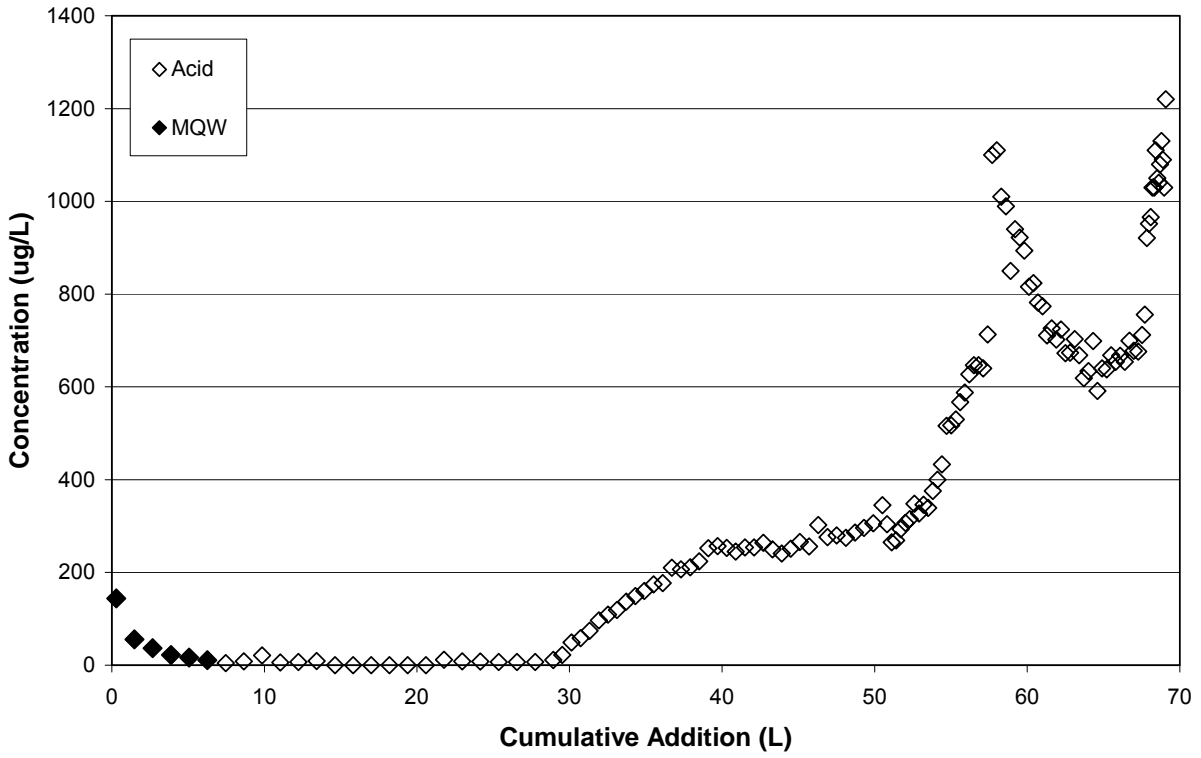


Figure 5. Concentration of Fe with cumulative leachate addition.

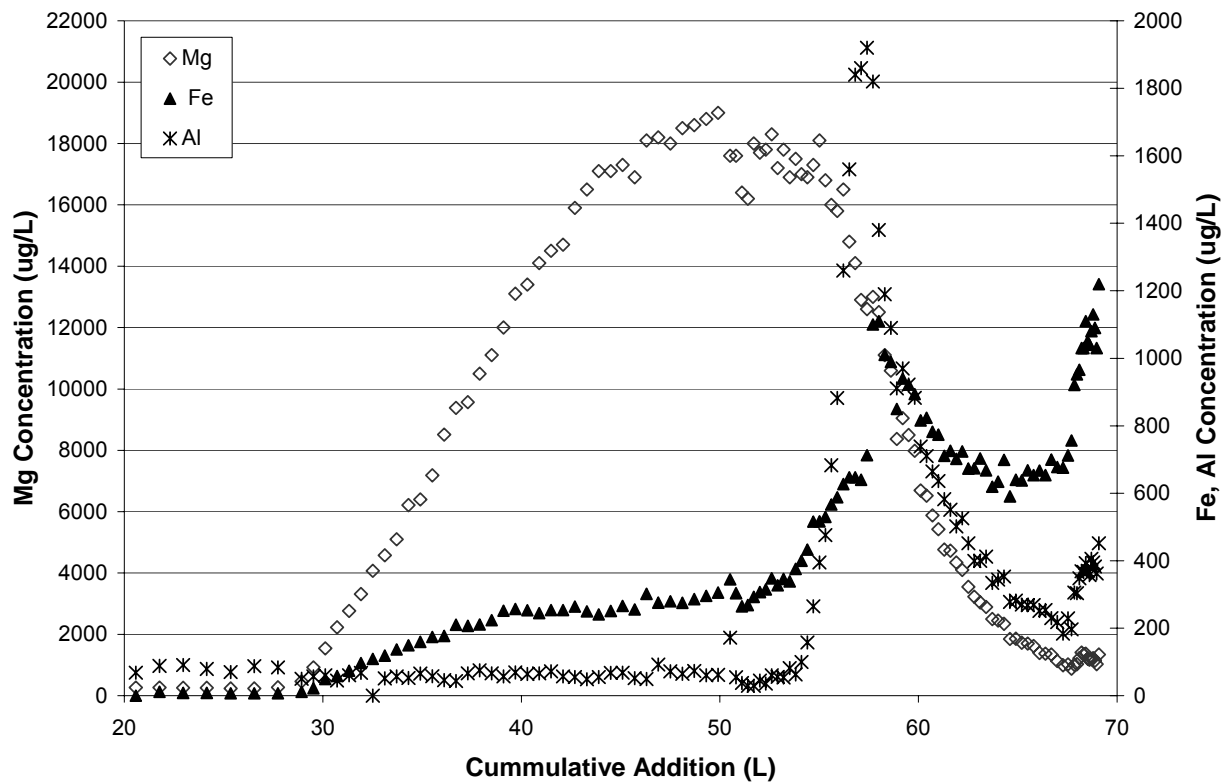


Figure 6. Concentration of Al, Fe and Mg with cumulative leachate addition

The post-leaching residue accounted for less than 2% of the original wallboard, with only traces of remaining gypsum, but higher concentrations of Fe and Al, as well as As, Ba, Co, Cr, Hg, Mo, Ni, Pb and Ti (discussed earlier). It appears that the phase responsible for retention of these metals is not the finer, high-surface-area calcium sulfate, but more likely an iron or mixed iron and aluminum phase.

Based on XRD analysis (Figure 7), the material is comprised mainly of amorphous material and quartz, with minor amounts of clay minerals. SEM-EDS analysis (Figure 8 a – c) indicates the presence of quartz crystals and fragments, aluminosilicates, iron-rich particles (bright areas of images), fly ash spheres and fragments, heat treated particles, and ceramic (fiberglass) and cellulose fibers. The ceramic and cellulose particles are likely additives introduced during the wallboard manufacturing process. The aluminosilicates could have been introduced during the manufacturing process or with the limestone in the FGD unit.

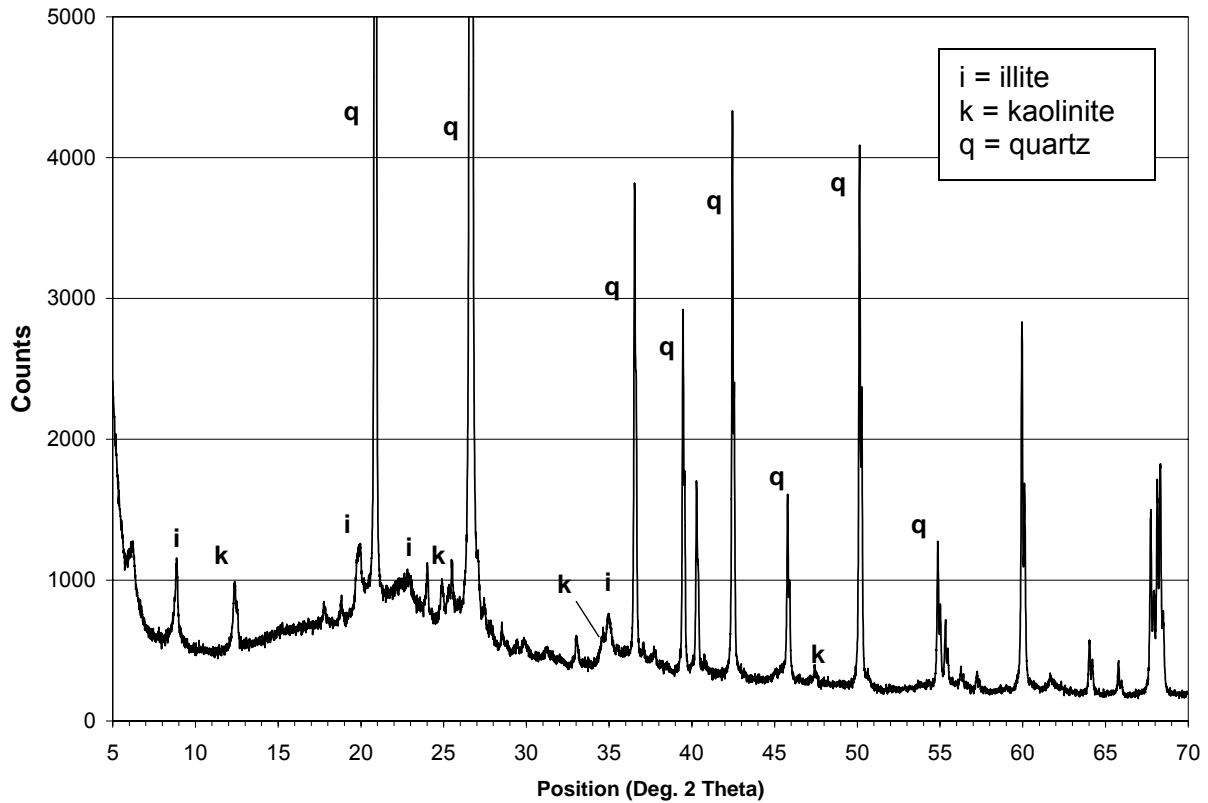


Figure 7. X-ray diffraction pattern of the post-leaching residue.

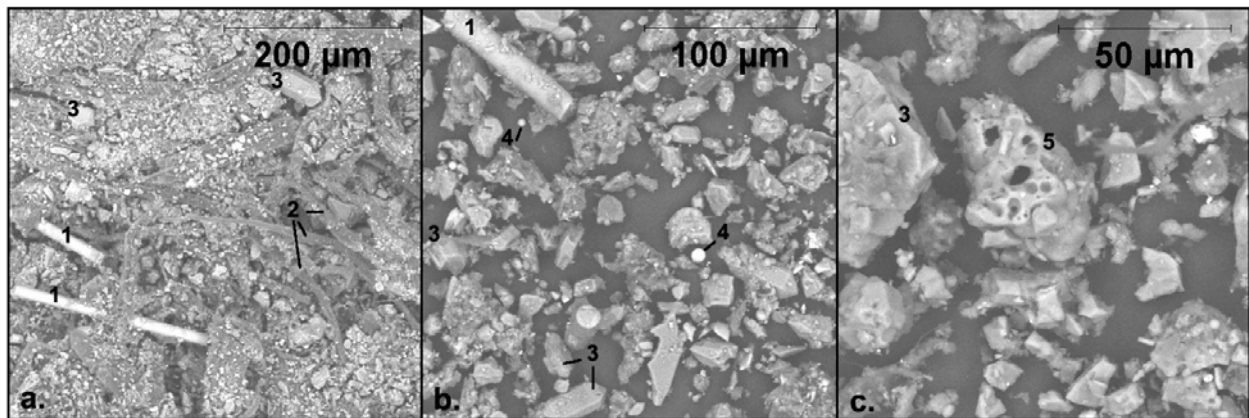


Figure 8a-c. SEM micrographs of the wallboard post-leaching residue. Examples of particle are labeled as follows: (1) ceramic fibers, (2) cellulose fibers, (3) quartz crystals and pieces, (4) fly ash spheres, and (5) heat-treated particles.

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 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.

Disclaimer: The mention of specific products names is to facilitate understanding and does not imply an endorsement by the U.S. government.

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