

# Leaching behavior of mineral processing waste: Comparison of batch and column investigations

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## Abstract

In this study, a comparison of laboratory batch and column experiments on metal release profile from a mineral processing waste (MPW) is presented. Batch (equilibrium) and column (dynamic) leaching tests were conducted on ground MPW at different liquid–solid ratios (LS) to determine the mechanisms controlling metal release. Additionally, the effect of pH on metal release is also discussed. It was observed that acidic pH conditions induced dissolution of As, Zn and Cu. Negligible leaching at alkaline pH was observed. However, Se depicted amphoteric behavior with high release at low and high pH. The batch and column data showed that As and Se release increased with LS ratio, while that of Cu and Zn increased initially and tapered towards equilibrium values at high LS ratios. The results on metal release from the MPW suggested that dissolution of the metal was the controlling mechanism. Leaching profiles from the batch and column data corresponded well for most LS ratios. This is most likely due to the acidic character of the waste, minimal changes in pH during the column operation and granular structure of the waste. From a waste management perspective, low cost batch equilibrium studies in lieu of high cost column experiments can be used for decision making on its disposal only when the waste exhibits characteristics similar to the mineral processing waste.

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**Keywords:** Mineral processing waste; Leaching; Metals; Liquid–solid ratio

## 1. Introduction

The release of toxic trace metals such as arsenic (As), selenium (Se) and zinc (Zn) from anthropogenic wastes at elevated concentrations is an environmental concern. Significant volumes of mining residues are deposited in waste dumps on the grounds in unpopulated areas by the mining companies, as a part of cost-saving efforts, resulting in apparent health problems due to metal release [1,2]. The mechanisms of trace metal release from mining and mineral processing waste (MPW) include weathering and/or oxidation of the mineral ores, dissolution under extreme reductive conditions and desorption from the surface [2–6]. Most MPWs are exempt from hazardous waste regulations under Resource Conservation and Recovery Act (RCRA) [7,8]. However, in select cases, the levels of As, Se and Zn, contami-

nating the local aquifers and soils is higher than those mandated by the U.S. Environmental Protection Agency (USEPA). Therefore, it is necessary to evaluate the fate and transport of the toxic metals in order to identify remediation techniques and control hazardous contamination.

The USEPA mandated procedures such as the Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) evaluate the effects of solid waste disposal in municipal landfills and ground water leaching based on groundwater quality limits. However, other physicochemical factors such as pH, redox and microbial activity are also known to affect metal mobility from solids [9–14]. Most metals exhibited increased leaching at low and high pH levels [9,10,12,15]. In addition, metal sequestration can occur due to secondary precipitation or adsorption reactions, changes in pH or a pH induced redox potential ( $E_h$ ) decrease could enhance metal mobility due to reductive dissolution. In addition, the variability in liquid–solid (LS) ratios (corresponding to a certain number of years in disposal conditions) may

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also affect the total amount of metals available for leaching [16–18].

The assessment of the potential of contaminant release from solid residues is usually achieved via static (batch) extraction tests or dynamic (column) tests, all of which have been extensively documented in literature [8,15–17,19–21]. Even though static tests are simple and provide qualitative predictive information on the leaching behavior, their use to evaluate potential metal release in landfill settings is still debatable. The utility of batch extraction tests may be limited as they do not adequately simulate long-term and intermittent leaching conditions in the field [17,21–23]. Previous research showed that the release behavior of metals observed in different testing conditions allowed to distinguish between two typical transfer mechanisms: (1) the pure diffusive transport for very soluble species, such as alkaline metals and (2) the dissolution process coupled with diffusion for most amphoteric metals [17–19,22,23]. Thus, the use of column studies to evaluate metal release is highly attractive as it served to monitor the metal release over longer durations and also identify temporal variations in the contaminant concentrations during the course of its transport through the waste.

The objectives of this study were (1) evaluate metal release as a function of pH and; (2) compare As, Se, Zn and Cu release in batch (static) and column tests as a function of LS ratio. The results obtained from the experiments were used to examine the effectiveness of the two methods (static and dynamic) as predictive tools for risk assessment of solid wastes.

## 2. Experimental

### 2.1. Materials

The MPW, obtained from mining and metallurgical operations, was used for the study, details of which are provided elsewhere [9,10]. The MPW used here was collected from the waste dumps located at different areas of abandoned mine site. Upon sample collection, the waste was homogenized and then used for this study. Once homogenized, the waste was sieved through U.S. standard No. 10 mesh (nominal opening of 2 mm) to obtain particles with sizes less than 2 mm. Acid extraction of metals using EPA method 3051 (microwave digestion in nitric acid) was performed to determine the total metal content in the waste [8]. The National Institute for Standards and Technology (NIST) soil reference standard (NIST 2710) was used for calculating recoveries of the metals in all digestions.

### 2.2. Static extraction tests

To evaluate the effect of LS ratio on metal release, static (batch) extractions using deionized water was performed on MPW at LS ratios of 5, 10, 20, and 50 L kg<sup>-1</sup> and rotated in a tumbler at 30 ± 2 rpm for 48 h. The extractions were performed under conditions similar to the TCLP, albeit at pH of 3. Metal release as a function of pH was determined by performing the generalized acid neutralization capacity (GANC) test, adapted from the Environment Canada Acid Neutralization Capacity (ANC) test [14,18]. The test involved several batch

Table 1  
Total concentration of metals (mg kg<sup>-1</sup>) in MPW

Metal	Total metal content (mg kg <sup>-1</sup> )
Arsenic (As)	471.4 ± 18.1
Copper (Cu)	1754.3 ± 43.8
Iron (Fe)	66271.4 ± 2620.5
Selenium (Se)	183.1 ± 26.3
Zinc (Zn)	429.2 ± 29.8

Data reported here is an average of 10 replicate acid digestions.

extractions using increasing strengths of glacial acetic acid and Ca(OH)<sub>2</sub> as base. The extractions followed the methodology of the TCLP test, albeit for 48 h duration. The pH of the suspension was monitored and the extract filtered at the end of the experiment for metal analysis.

### 2.3. Column tests

Kinetic column leaching tests were performed in plexiglass columns (3.81 cm diameter and 7.62 cm height with 35 μm pore size supports). The column was operated in the up flow configuration to avoid channeling and plugging. The extraction fluid (deionized water containing sodium azide to prevent biological growth) was fed to the columns at a rate of 60 ml per day. Prior to starting the test, the extraction fluid was pumped to ensure efficient and appropriate distribution of the solid and liquid phases in the system. Two separate tests using multiple columns operated in series, containing the exact amount of wastes in each column, was performed. Samples were collected periodically in an effort to vary LS ratios from 0.13 to 21.3 L kg<sup>-1</sup> for the two columns study (26 days duration) and 0.14–22.73 L kg<sup>-1</sup> for the three columns (26 days duration). The effluent from the columns passed through in-line *E<sub>h</sub>* (redox potential) and pH probes (Cole Parmer, IL), and the data continuously recorded with the help of a data logger (Prober-PH8, version 2.0, Cole Parmer, IL). The extracts were collected at regular intervals and filtered through 0.45 μm pore size nylon (Whatman, IL) filters for metal analysis.

### 2.4. Analytical methods

The extract metal concentration was analyzed using an inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid, Thermo Electron Corporation, CA), in accordance with EPA Method 6010B [8]. The instrument detection limits (IDLs) were 12 μg L<sup>-1</sup> for As, 10 μg L<sup>-1</sup> for Cu and Se, 58 μg L<sup>-1</sup> for Fe and 53 μg L<sup>-1</sup> for Zn.

## 3. Results and discussion

### 3.1. Characteristics of MPW

Acid extractions (EPA Method 3051) revealed that the MPW contained relatively high concentrations of copper (Cu, 1754.3 mg kg<sup>-1</sup>) and iron (Fe, 66271.4 mg kg<sup>-1</sup>); and moderate levels of arsenic (As, 471.4 mg kg<sup>-1</sup>), selenium (Se, 183.1 mg kg<sup>-1</sup>), and zinc (Zn, 429.2 mg kg<sup>-1</sup>) (Table 1). The

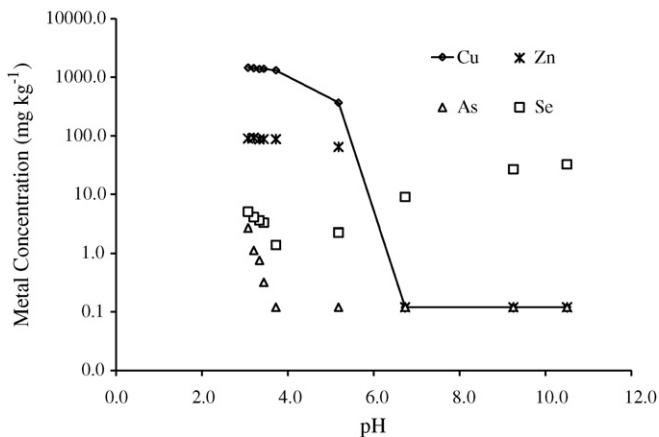


Fig. 1. Metal release as a function of pH determined by GANC tests.

% recovery for the NIST 2710 standard (calculated as the ratio of measured metal concentration (in  $\text{mg kg}^{-1}$ ) to the certified values) ranged from 88% for Fe to 107% for As. In our previous work [9,10], we had reported that As, Se and Zn were mostly associated in the less mobile iron oxide or the sulfidic fractions (determined by sequential extraction procedures). On the other hand, easily mobile Cu fraction was higher (almost 50%). The mineralogical composition, determined by X-ray diffraction (XRD) analysis, was observed to be hematite and silicon dioxide (quartz) as the predominant crystalline phases.

### 3.2. Batch extractions: effect of pH

The release profile of As, Se, Cu and Zn as a function of pH suggested that metal solubilization occurred mainly due to acid attack (Fig. 1). Among the divalent metal cations, almost 83% ( $1456 \text{ mg kg}^{-1}$ ) of Cu leached from the MPW at  $\text{pH} < 4$ , while that for Zn was about 20% ( $90 \text{ mg kg}^{-1}$ ). With increasing pH, metal solubility decreased precipitously to almost non-detect levels and can be attributed to metal precipitation as hydroxides. Arsenic release profile was also similar to that of Cu and Zn, albeit at relatively low concentrations even at acidic pH. The decrease in As concentrations at elevated pH may be due to the adsorption/co-precipitation of redox sensitive As with precipitated iron hydroxides [10,15,24]. The dissolution of As, Cu and Zn at low pH followed by adsorption/co-precipitation reactions at alkaline pH appeared to be the mechanisms controlling metal release from the MPW. On the other hand, Se extract concentrations were observed to decrease initially with pH increase to 4. With further increase in pH, the extract concentration increased significantly from  $1.38 \text{ mg kg}^{-1}$  (pH 3.7) to  $32.4 \text{ mg kg}^{-1}$  at alkaline pH, thus showing amphoteric behavior. This increase may possibly be due to the oxidation to a more water soluble species (Se (VI)), which is more likely to desorb under alkaline pH conditions [9,24,25].

### 3.3. Batch extractions: effect of LS ratio

The effect of LS ratio on metal release indicates the prevalence of the dominant mechanism, either solubility or

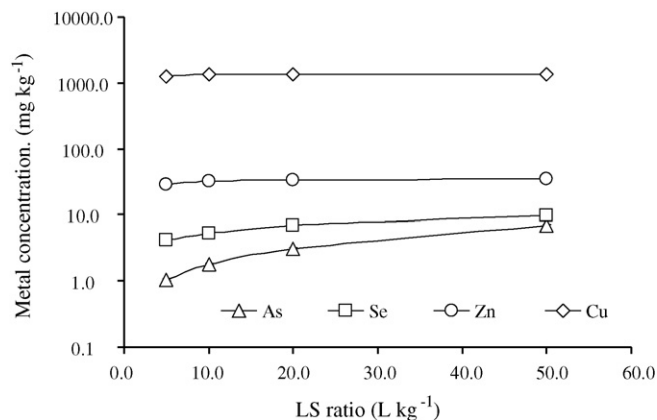


Fig. 2. Metal release as a function of LS ratio (batch tests).

diffusion-controlled. The batch extraction data (Fig. 2) indicated that Cu and Zn solubilities were independent of the LS ratio. In the case of Cu, the metal release increased from 1236 to  $1360 \text{ mg kg}^{-1}$ , as the LS ratio increased from 5 to  $10 \text{ L kg}^{-1}$ . Further increase in LS ratio decreased the metal release marginally to  $1328.3 \text{ mg kg}^{-1}$ . At LS ratio of  $10 \text{ L kg}^{-1}$ , Cu and Zn leach to maximum concentrations. The data indicated that the metals reached equilibrium with respect to LS ratio, indicating that the available fraction of metal leached at this LS ratio. With increasing LS ratio, the high amounts of the liquid phase results in some dilution of the metal concentration, resulting in marginally decreased extract concentrations. Since the pH of the suspension was recorded to be about 3.1, such high Cu solubilities can be attributed to its dissolution at low pH. On the other hand, a moderate increase in As and Se release was observed with increasing LS ratio, with the leached amounts less than 10% of the total metal concentration. This increase in extract concentration with increasing LS ratio suggested dissolution mechanisms [16–18].

### 3.4. Column tests: effect of LS ratio

Kinetic studies on metal leaching from MPW were performed in two separate experiments, wherein the columns containing the waste were lined sequentially. The advantages of this procedure was that it provided information on the variability in extract concentration when it comes in contact with another dry solid, in addition to providing information on the effect of LS ratio on metal mobility. Since the flow rate of the extraction fluid was fixed, the LS ratio is directly proportional to the retention time. Therefore, higher LS ratios corresponded to longer durations and simulated conditions to observed long-term leaching patterns. The pH of the extract was monitored in each column and was observed to be in the range of 3.5–4.2, while the redox potential was in the range of 390–450 mV, making the system highly toxic and acidic. Even though XRD analysis could not detect any sulfidic phases, the presence of sulfides in the matrix (probably present in minor amounts) could possibly explain the low pH. The cumulative leached amounts were calculated as given below in Eq. (1), where,  $C_L$  is the cumulative leached amount ( $\text{mg kg}^{-1}$  dry sample),  $V_i$  is the volume of the collected fraction (L),  $C_i$  is

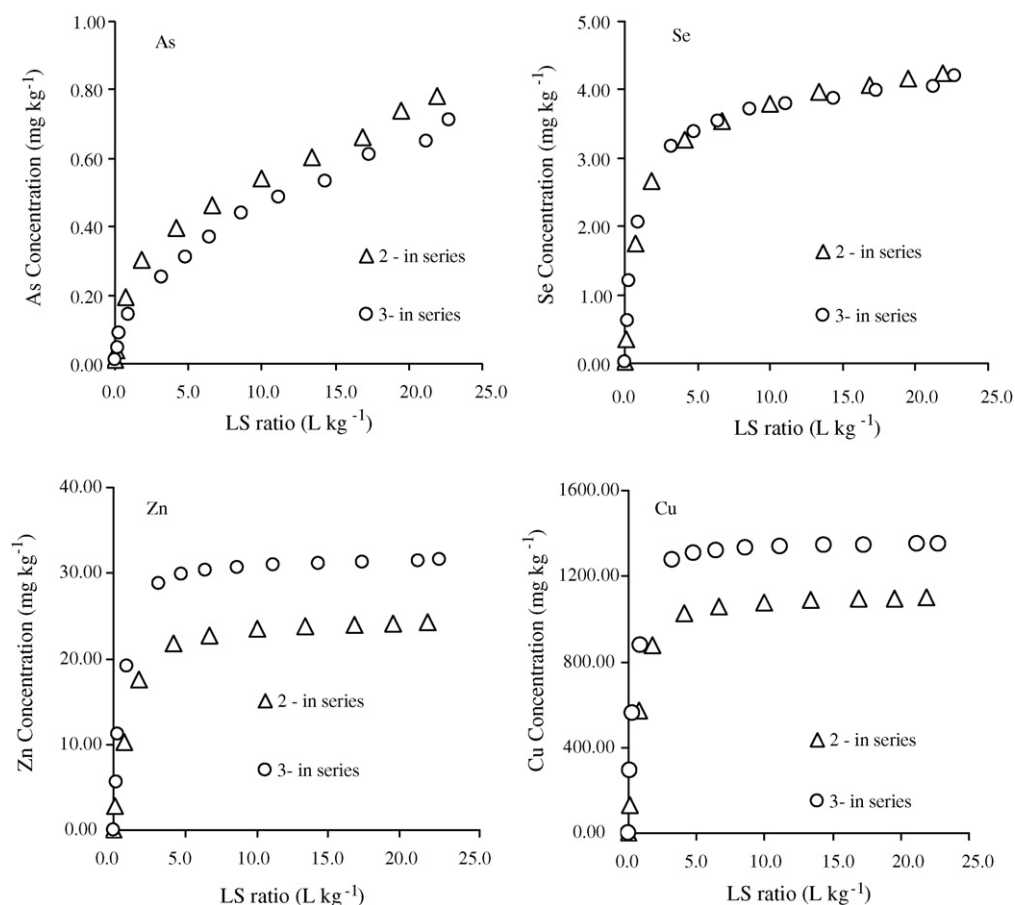


Fig. 3. Metal release as a function of LS ratio (column tests).

the concentration of the relevant species in the fraction ( $\text{mg L}^{-1}$ ) and  $M_{\text{column}}$  is the mass of test material in the column ( $\text{kg dry sample}$ ).

$$C_L = \frac{\sum V_i C_i}{M_{\text{column}}} \quad (1)$$

As can be seen in Fig. 3, cumulative metal concentrations in the extract were observed to increase with LS ratio, indicating that metals would probably leach in greater amounts, if exposed for longer durations. As and Se concentrations in the extract increased continuously with LS ratio, typical of dissolution of the solid phase under acidic conditions [10,11,16]. The increase in As and Se release till the termination of the experiment indicated that surface dissolution of the metals is still the prevailing mechanism for leaching. As the extract passed from one column to the next, the extract concentration decreased marginally for arsenic, which could be attributed to its adsorption on the iron oxides in the waste. Iron oxides have a greater affinity for As adsorption at low pH values [24,25]. Such a phenomenon was not observed for Se, as the extract concentration was similar in both the two column and three column operations.

Cu and Zn leached almost linearly with increasing LS ratios at low LS ratios. Beyond the LS ratio of 6.5, the extract metal concentration tapered to almost equilibrium values. Initially, metal release at low LS ratios is usually controlled by dissolution mechanisms. However, once the metals are removed from

the surface, its release is purely governed by diffusive transport due to a concentration gradient [16,18]. Cu and Zn leaching profiles as a function of LS ratio is characteristic of contaminant release of percolation tests, as observed previously in literature [16,18]. The equilibration of the leaching profile for Cu and Zn at high LS ratios can be attributed to reduced availability of the metal following their initial solubilization. Unlike As and Se, leaching of Cu and Zn was almost 1.25-fold higher in the three column operation, compared to the two column experiment, due to the increased mass of the waste in the system which resulted in greater availability of the metals. Thus, based on the column studies, it can be concluded that oxyanionic metals such as the release of As and Se is more likely to be influenced by dissolution mechanisms and the pH of the extraction fluid, while that of the divalent metals is dependent on the availability of the metals in the solid waste. A comparison of the metal release profiles in the batch and the column tests indicated that metal release profiles in the batch test corresponded well with the column tests, albeit at different concentrations. This is possibly due to the difference in the experimental procedure (over end tumbling for batch tests as opposed to preferential flow for the column tests).

#### 4. Conclusion

Metal leaching from MPW was investigated under equilibrium (batch, constant pH) and dynamic (column studies). It was

observed that As, Cu and Zn showed high leaching in acidic pH, while Se showed “V” shaped leaching profile with respect to pH. Batch data as a function of LS ratio indicated that dissolution mechanisms contributed to metal release, which corresponded well with the column data. The leaching of Cu and Zn was independent of LS ratio at high values, while that of As and Se was dependent on LS ratio. More than 70% of Cu leached in less than 26 days (or LS ratio of 20 L kg<sup>-1</sup>), while the release of As, Se and Zn was less than 10%. Overall, the estimated long-term leachate concentration is expected to be higher for As and Se with very high LS ratio (>100 L kg<sup>-1</sup>), while that of Cu and Zn would either saturate or decrease. High initial leaching at low LS ratios can be attributed to the acidic nature of the granular waste. Care should be taken in interpreting the maximum leachability of the metals as batch test could significantly overestimate potential release due to negligible mass transfer limitations and absence of other geological and hydrological factors.

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