

# An Investigation of the Partitioning of Metals in Mine Wastes Using Sequential Extractions

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## ABSTRACT

The mode of occurrence of metals in mine wastes is investigated using sequential extractions. Metals are extracted from some or all of seven operationally-defined phases: water-soluble, ion-exchangeable, carbonate, amorphous Fe-oxide, crystalline Fe-oxide, sulfide, and silicate. The quantity of metals extracted from each phase varies with particle size. The presence of jarosite (potassium end-member formula,  $KFe_3[SO_4]_2[OH]_6$ ) influences the selection of the procedure for extracting the crystalline Fe-oxide phase. Anglesite ( $PbSO_4$ ) and cerussite ( $PbCO_3$ ) are extracted as several phases. Extraction results can be explained only in part by X-ray diffraction (XRD) mineralogy because of lack of specificity of the extraction procedures, relatively high XRD detection limits, and the presence of 40% XRD-amorphous matter in each waste. The increasing chemical strength of the sequentially applied methods provides a basis for judging metal availability, water-soluble metals being most available and silicate-bound metals being least available.

## INTRODUCTION

Sequential extractions have been used primarily for the chemical speciation of metals in soils and sediments. Tessier et al. 1979, maintained that sequential extractions can furnish detailed information about the mode of occurrence, biological availability, and mobilization of trace metals in sediments. Accordingly, when applied to mine wastes, the extractions may provide information useful for evaluating the near and long term effects of wastes on the environment.

In sequential extractions, metals are extracted from mineral phases that are operationally defined. This means that the procedure itself defines the extracted phase. A procedure that preferentially extracts metals associated with any one mineral or component of the sample is often referred to as phase specific, although total specificity is highly improbable if not impossible. Commonly, metals are extracted from several, or all of the following operationally-defined phases and in the given order: (1) metals present in water-soluble form; (2) ion-exchangeable metals; (3) metals associated with carbonates; (4) metals associated with amorphous iron and manganese oxides ( $Fe-MnOx_{am}$ ); (5) metals bound to crystalline iron oxides ( $FeOx_{crist}$ ); (6) metals occurring as, or in sulfides; and (7) the remaining metals not extracted in the preceding steps, referred to as the silicate or resistate phase. A step for the extraction of metals associated with organic material is sometimes included early in the sequence.

The partitioning of metals in four acid-generating mine wastes was investigated using sequential extractions. Concurrently, the wastes were mineralogically characterized by X-ray diffraction (XRD). Extractions were conducted on composite samples collected from the surface of waste dumps of the May Day and Yukon mines in the upper Animas Basin, near Silverton, Colorado, and the Sunday No. 2 and Venir mines near Leadville, Colorado. Sampling of the dumps and preparation of the bulk samples are described elsewhere (Smith et al. this volume). Extractions were first conducted on five size fractions derived from the <2mm fraction of the composites (table 1) and on several types of jarosite, a mineral commonly associated

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with pyritic mine wastes. The initial extractions were conducted to evaluate particle size effects as well as to establish the phase of extraction of jarosite, which was identified in all of the composites by XRD. For expediency, in these initial extractions metals were extracted from only five of the seven phases enumerated above. The ion-exchangeable and carbonate phases were not extracted and any metals associated with these phases are presumed to have been extracted with the  $\text{Fe-MnOx}_{\text{am}}$  phase. Aside from the water-soluble phase, the procedures used for the initial extractions are recommended by Griffioen and Broers 1993 (table 2).

Based on the results of the initial extractions, a second set of extractions was performed directly on the  $<2\text{mm}$  fraction of the composites and on two types of jarosite. All samples were pulverized to  $<0.075\text{mm}$ . The number of phases extracted was expanded to include the ion-exchangeable and carbonate-associated metals and different procedures were used to extract the  $\text{FeOx}_{\text{cryst}}$ , sulfide, and silicate phases (table 3). Finally, extractions of the first five phases (water-soluble through  $\text{FeOx}_{\text{cryst}}$ ) were applied to samples of anglesite ( $\text{PbSO}_4$ ) and cerussite ( $\text{PbCO}_3$ ), Pb minerals identified in specially prepared mineral separates of the wastes in detailed XRD studies (Sutley and Desborough, this volume).

## METHODS

### Extractions of Varying Size Fractions and Jarosites

Initially, to evaluate particle size effects, five phases were extracted from five size fractions (table 1) of each mine waste composite using the procedures in table 2. To determine the phase of extraction of jarosite, the same procedures were applied to samples of potassium, hydronium, and lead jarosite. The size fractions were obtained by sieving the bulk  $<2\text{mm}$  fraction of the composites through nested stainless steel sieves. The particle size of the jarosite samples was estimated to be  $<0.18\text{mm}$ . Following each procedure, the extraction solution was separated from the sample residue by high speed (12,500 rpm), temperature-controlled ( $20\text{--}25^\circ\text{C}$ ) centrifugation and the extraction solution was filtered through a  $0.45\mu\text{m}$  cellulose membrane syringe filter. The extract solutions were analyzed for metals by inductively coupled plasma-atomic emission spectrometry (ICP-AES) or by atomic absorption spectrophotometry (AAS).

### Seven-step Extraction Procedure

Following the above initial extractions, the seven-step extraction procedure in table 3 was performed on splits of the  $<2\text{mm}$  fraction of the composites and on samples of potassium and lead jarosite. In addition, steps 1 through 5 were applied to samples of anglesite and cerussite. For these extractions, the samples were finely ground to  $<0.075\text{mm}$  in a miniature grinding mill or with a mortar and pestle. Separation of the sample residue from the extract solution was by centrifugation, as above. To assist in this separation and preclude further separation by filtration, pure silica gel was added to the sample prior to extraction of the initial ( $\text{H}_2\text{O}$ -soluble) phase. The use of silica gel is permitted if analysis of the extract solutions for Si is not requisite. The extract solutions were analyzed for metal content by ICP-AES or AAS.

**Table 1 Size fractions of composites and weight percent of total composite weight**

Fraction	Range of particle size	Weight percent of Composite	Weight percent of Composite
		May Day	Yukon
1	$<2\text{mm} >0.425\text{mm}$	62.45	55.40
2	$<0.425\text{mm} >0.125\text{mm}$	21.22	27.31
3	$<0.125\text{mm} >0.075\text{mm}$	8.37	8.95
4	$<0.075\text{mm} >0.043\text{mm}$	7.10	7.57
5	$<0.043\text{mm}$	0.86	0.77
		Sunday No.2	Venir
1	$<2\text{mm} >0.425\text{mm}$	63.50	55.08
2	$<0.425\text{mm} >0.125\text{mm}$	22.73	25.74
3	$<0.125\text{mm} >0.075\text{mm}$	9.04	12.42
4	$<0.075\text{mm} >0.043\text{mm}$	4.40	6.44
5	$<0.043\text{mm}$	0.33	0.33

**Table 2 Five-procedure sequential extraction applied to five size fractions of mine waste composites and samples of jarosite (steps 2-5 are recommended by Griffioen and Broers,1993)**

Phase	Description of Procedure
Water-soluble	1. One gram of sample is extracted with 20ml deionized water in a 50ml centrifuge tube for two hours in a horizontal, reciprocating shaker, at ambient temperature.
Fe-MnOx <sub>am</sub>	2. The residue from no. 1 is extracted with 20ml of 0.25M hydroxylamine hydrochloride in 0.25M HCl for 30 minutes in a water bath, at 50°C (Chao and Zhou 1983).
FeOx <sub>cryst</sub>	3. The residue from no. 2 is extracted with 40ml of a solution that is 0.2M in ammonium oxalate and oxalic acid and 0.1M in ascorbic acid for two hours in a water bath, at 94°C.
Silicate	4. The residue from no. 3 is shaken for eight hours with 30ml of 10M HF to which is then added 5g of boric acid and the sample is shaken for another 8 hours.
Sulfide	5. The residue from no. 4 is shaken for two hours with 10ml concentrated HNO <sub>3</sub> . Prior to centrifugation, 15ml of deionized water are added (Lord 1982).

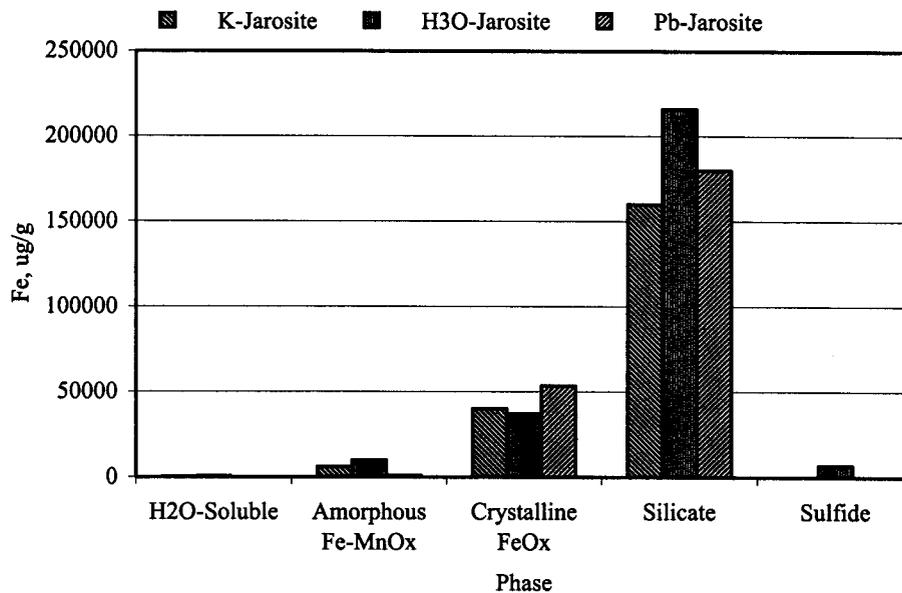
**Table 3 Seven-procedure sequential extraction applied to the <2mm fraction of the mine waste composites and samples of jarosite**

Phase	Description of Procedure
Water-soluble	1. Same as for 5-procedure extraction except 0.25g of sample, with 0.25g of silica gel added, is extracted with 25ml of water.
Ion-exchangeable	2. The residue from no. 1 is extracted with 25ml 1M sodium acetate for one hour in a horizontal reciprocating shaker, at ambient temperature.
Carbonate	3. The residue from no. 2 is extracted in a shaker for two hours with 25ml 1M sodium acetate buffered to pH.5 with acetic acid.
Fe-MnOx <sub>am</sub>	4. The residue from no. 1 is extracted with 25ml of 0.25M hydroxylamine hydrochloride in 0.25M HCl for 30 minutes in a water bath, at 50°C (Chao and Zhou 1983).
FeOx <sub>cryst</sub>	5. The residue from no. 4 is extracted with 25ml 4M HCl for 30 minutes in a water bath at 94°C.
Sulfide	6. Two grams of sodium chlorate are added to the residue from no. 5, followed by careful addition of 10ml concentrated HCl. After 45 minutes the aqueous phase is separated and diluted to 25ml with deionized water. The residue is extracted for 40 minutes with 25ml 4M HNO <sub>3</sub> in a boiling water bath. The two extracts are analyzed separately and the results combined. (Chao and Sanzalone 1977)
Silicate	7. The residue from no. 6 is transferred to a Teflon beaker and is digested with 10ml, of each, concentrated HNO <sub>3</sub> , HClO <sub>4</sub> , and HF at 220°C, to a moist bead. The moist bead is taken up in 25ml 4M HCl at 100°C for 30 minutes. The final volume is adjusted to 25ml with deionized water.

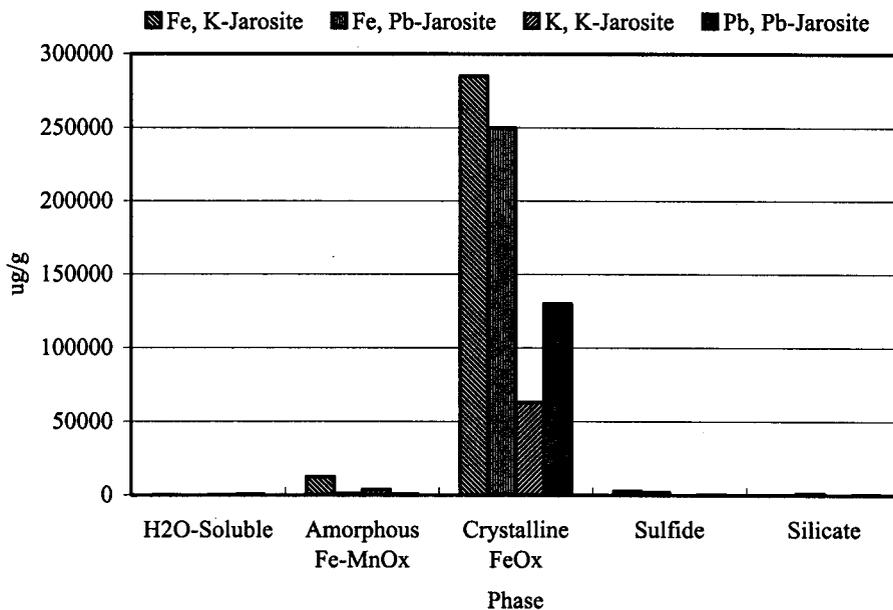
## RESULTS AND DISCUSSION

### Mineralogical Effects

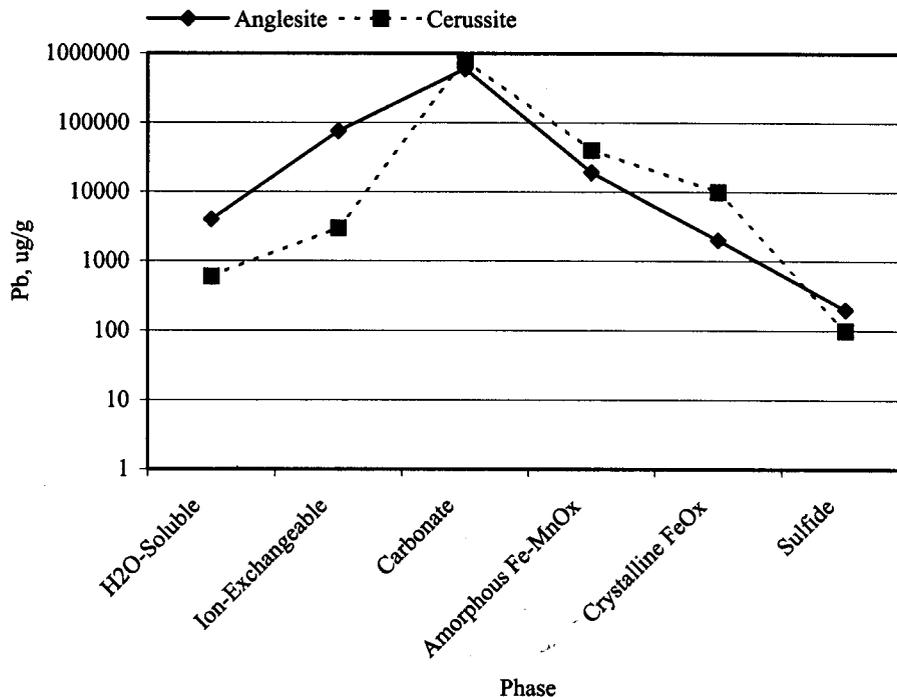
Differences in mineralogical composition influence selection of procedures commonly used for extraction of metals from phases of soils and sediments when they are applied to extraction of mine wastes. For example, the composites from the May Day, Yukon, Sunday No. 2, and Venir dumps were all determined by XRD to contain jarosite, a mineral of the general formula  $AFe_3(SO_4)_2(OH)_6$ . The "A" position is occupied by any of a number of cations, most often  $K^+$ ,  $Na^+$ ,  $H_3O^+$ , and  $Pb^{2+}$ . In this study, several types of jarosite were sequentially extracted using the procedures recommended by Griffioen and Broers 1993 for extraction of soils and sediments. These include a solution of ammonium oxalate, oxalic acid, and ascorbic acid for extraction of the FeOx<sub>cryst</sub> phase, HF and H<sub>3</sub>BO<sub>3</sub> for extraction of the silicate phase, and HNO<sub>3</sub> to extract the sulfide phase (table 2). The results for Fe in figure 1 show that three types of jarosite (potassium, hydronium and lead) are partially extracted by the solution used to extract the FeOx<sub>cryst</sub> phase but are mostly extracted by the solution used to extract the residual or silicate phase. On the other hand, based on the Fe, K and Pb results shown in figure 2, K- and Pb-jarosite are almost totally extracted by hot 4M HCl. The use of HCl



**Figure 1 Fe in five operationally-defined phases extracted from three types of jarosite following the procedures in table 2**



**Figure 2 Fe and K in five operationally-defined phases of K-jarosite and Fe and Pb in five operationally-defined phases of Pb-jarosite extracted using procedures described in table 3**



**Figure 3 Pb in six operationally-defined phases extracted from anglesite and cerussite**

of varying concentrations for extracting different crystalline Fe-oxide minerals, and its limitations, are noted by Chao 1984. Because of its effectiveness for extracting jarosite almost completely with the  $\text{FeOx}_{\text{cryst}}$  phase, the use of HCl is preferred for extractions of these mine wastes.

Figure 3 shows the results for Pb from the sequential extraction of anglesite,  $\text{PbSO}_4$ , and cerussite,  $\text{PbCO}_3$ . The results indicate that extraction of these minerals from mine wastes can be expected to begin with extraction of the water-soluble phase and conclude with extraction of the  $\text{FeOx}_{\text{cryst}}$  phase. The results show that anglesite is more water soluble than cerussite.

#### **The Effect of Particle Size**

The extraction of metals varies with particle size but not necessarily systematically. In general, the concentrations of water-soluble Fe, Pb, Zn and Cu increase with decreasing particle size for all the mine waste composites, although increases may be minor. This is shown for the May Day composite in figure 4. The concentration of metals extracted with the  $\text{Fe-MnOx}_{\text{am}}$  phase also increases with decreasing particle size. There is an inverse correlation of Fe and Zn in the  $\text{FeOx}_{\text{cryst}}$  phase and the size fractions of the Yukon composite (figure 5), while Pb is shown to increase in the mid-range size fractions and then decrease in concentration with decreasing particle size. In the sulfide phase, there is an overall positive correlation between particle size and the concentration of Fe, Pb, Zn and Cu in the Yukon composite (figure 6). A clear exception is the amount of Fe extracted from the fraction of largest particle size. The relatively low concentration of Fe extracted in the  $<2\text{mm} > 0.425\text{mm}$  fraction is attributed to incomplete dissolution of larger pyrite crystals under the conditions of extraction with nitric acid (Lord, 1982). The distribution of metals in the  $\text{FeOx}_{\text{cryst}}$  and sulfide phases of the Yukon composite (figures 5 and 6) is attributed to

increased oxidation of pyrite by weathering with decreasing particle size and the resulting increase in the amount of oxides in the smaller size fractions.

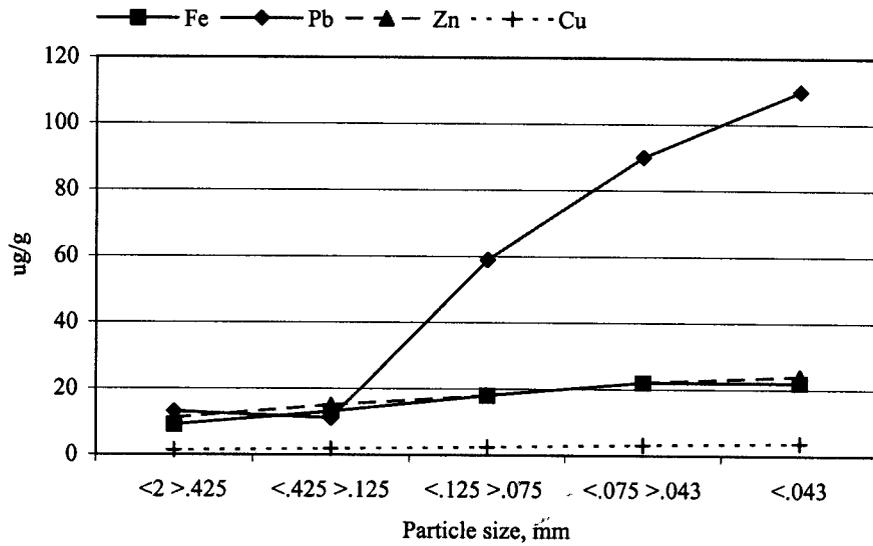


Figure 4 The effect of particle size on extraction of water-soluble metals, May Day composite

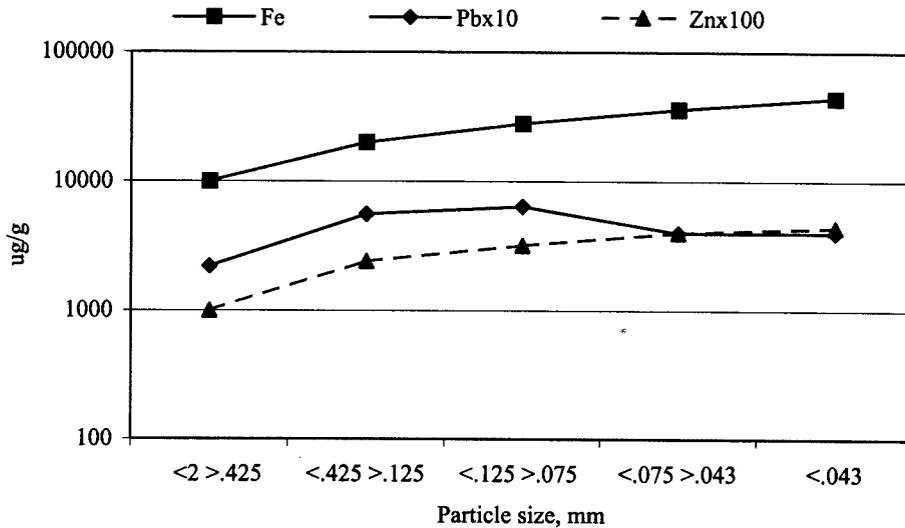
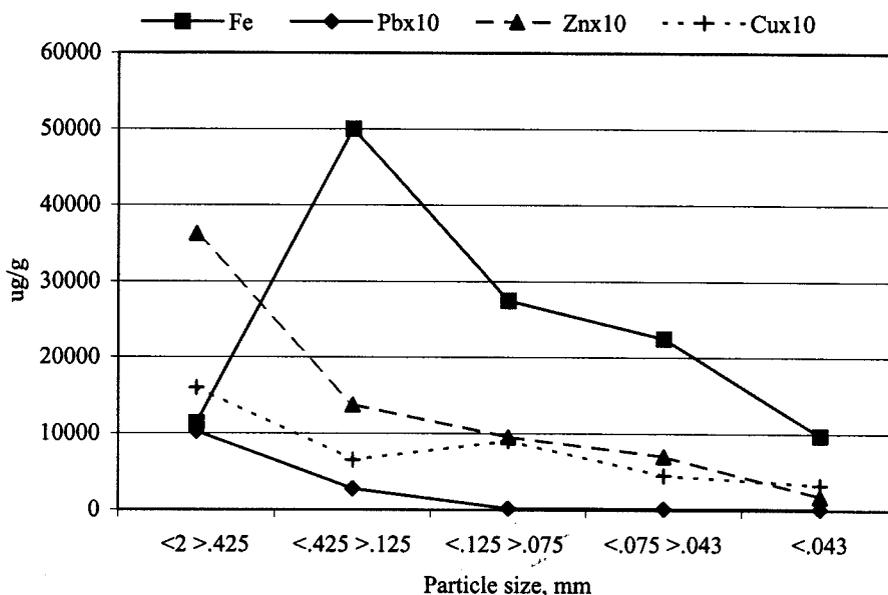


Figure 5 The effect of particle size on extraction of metals in the FeO<sub>x</sub><sub>cryst</sub> phase, Yukon composite

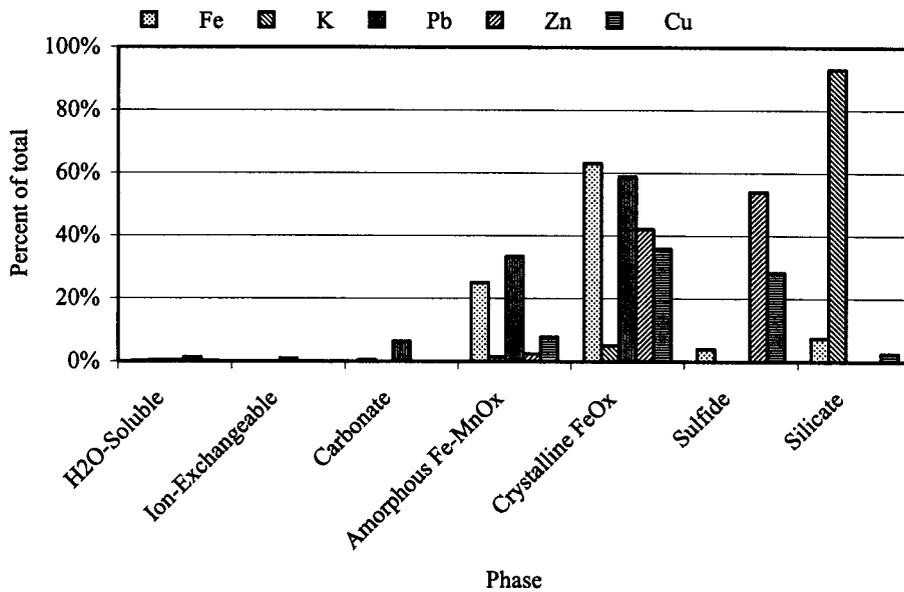


**Figure 6** The effect of particle size on extraction of metals in the sulfide phase, Yukon composite

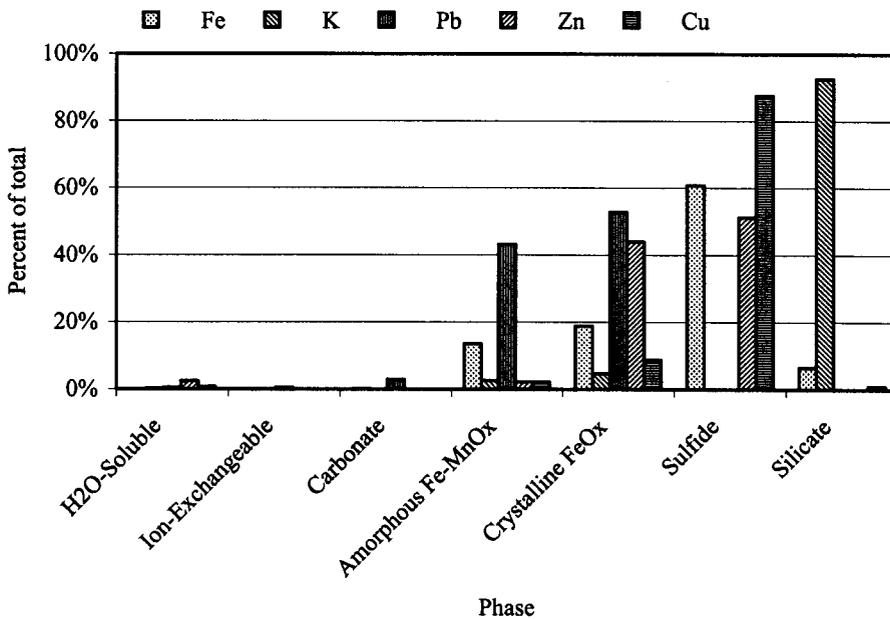
#### Partitioning of Metals in the <2mm Fraction of Mine Wastes

Results from the extractions of the <2mm fraction of the composites are shown in figures 7-10. Zinc and Cu are more favorably partitioned in the  $\text{FeOx}_{\text{cryst}}$  and sulfide phases of the composites while Pb appears to be more favorably partitioned in the  $\text{Fe}_{\text{am}}$  and  $\text{FeOx}_{\text{cryst}}$  phases. Lead minerals identified in the composites by XRD include anglesite, cerussite, and galena. As noted above, anglesite and cerussite are extracted over five phases and galena ( $\text{PbS}$ ) is soluble in HCl, the extract solution for  $\text{FeOx}_{\text{cryst}}$ . Iron is strongly partitioned into the  $\text{FeOx}_{\text{cryst}}$  phase of the May Day composite and the sulfide phase of the Yukon composite (figures 7 and 8). Differences between Fe in the  $\text{FeOx}_{\text{cryst}}$  and sulfide phases are less pronounced in the Sunday No.2 and Venir composites (figures 9 and 10). From figures 7-10, it is clear that in all the composites, K occurs almost exclusively in the silicate, or resistate phase, most likely in muscovite.

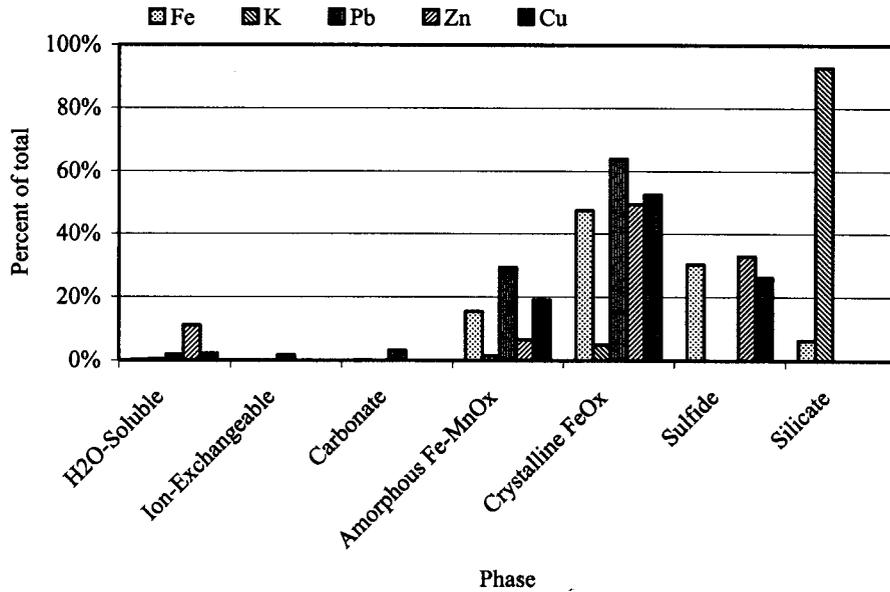
Semi-quantitative XRD analysis (Sutley and Desborough, this publication) shows the amount of jarosite in the four composites ranges from about 5 to 8 %. The amount of Fe extracted in the  $\text{FeOx}_{\text{cryst}}$  phase (figures 7-10) exceeds the amount of Fe accounted for by the XRD-jarosite in each composite. Host minerals of Fe not accounted for by jarosite are uncertain. Similarly, the occurrence of Fe in the sulfide phase of the Yukon, Sunday No.2 and Venir composites (figures 8, 9 and 10) exceeds the amount accounted for by XRD pyrite. The remaining sulfide-Fe is unaccounted for mineralogically. The amount of Fe extracted from the sulfide phase of the May Day composite (figure 7) equates to <0.5% pyrite, which was not detected by XRD. The occurrence of trace amounts of sphalerite,  $\text{ZnS}$ , in the May Day and Sunday #2 composites is reflected by Zn extracted with the sulfide phase (figures 7 and 9). Lead occurring in finely crystalline galena (<0.050mm), detected in a heavy mineral concentrate of the Sunday No.2 composite, was mostly extracted by 4M HCl with the  $\text{FeOx}_{\text{cryst}}$  phase. Extraction of anglesite,  $\text{PbSO}_4$ , found to be present in heavy mineral concentrates



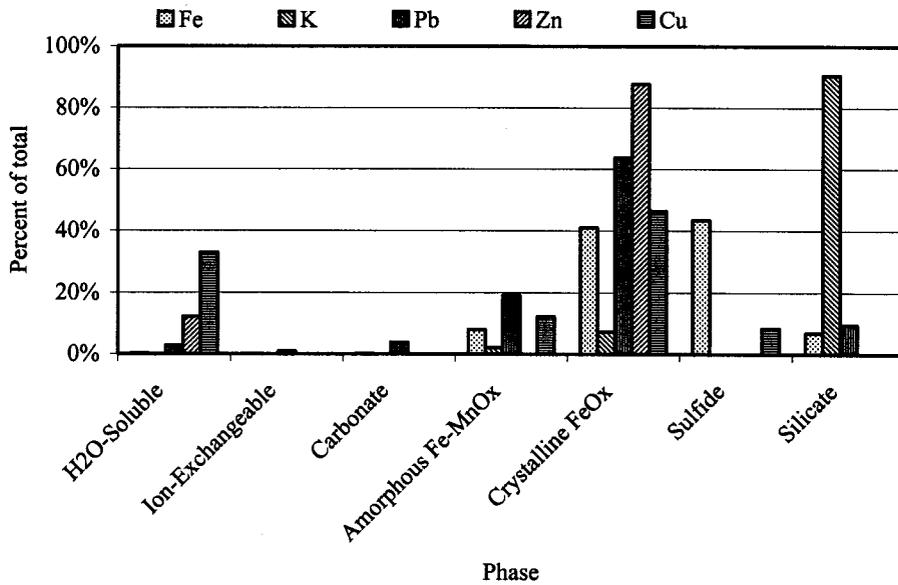
**Figure 7** The extraction of metals in seven phases of the <2mm size fraction, May Day composite



**Figure 8** The extraction of metals in seven phases of the <2mm size fraction, Yukon composite



**Figure 9** The extraction of metals in seven phases of the <2mm size fraction, Sunday No.2 composite



**Figure 10** The extraction of metals in seven phases of the <2mm size fraction, Venir composite

of the May Day and Venir composites, and cerussite,  $\text{PbCO}_3$ , in the Sunday No.2 composite probably spans extraction of the water-soluble through the  $\text{FeOx}_{\text{cryst}}$  phases, suggested by results of extractions of the pure minerals (figure 6). The amount of K extracted from the composites (figures 7-10), almost exclusively in the silicate phase, is not totally accounted for by muscovite or feldspar identified by XRD.

Mineralogical analysis of the May Day, Yukon, Sunday No.2 and Venir composites indicates that about 40% of each is amorphous material (Sutley and Desborough, this publication). Comparing the chemical composition derived from XRD mineralogy with the composition derived by other methods, including X-ray fluorescence (XRF) and analysis by ICP-AES and AAS following total digestion, shows that mineralogy does not account for significant amounts of Si, K, Al, and Fe. This implies that the unaccounted for portions of these metals reside in an amorphous phase. The results for the extraction of K shown in figures 7-10 suggest that it resides principally in an amorphous silicate phase.

#### Extraction Results and the Mobility and Availability of Metals

The progressively increasing rigor or strength of the procedures in sequential extractions provides a means for evaluating the mobility of metals in mine wastes and their availability to the environment. Defining as mobile, or potentially mobile, the metals extracted with the water-soluble through the  $\text{Fe}_{\text{am}}$  phases, table 4 shows the amount of mobile, Pb, Zn, and Cu in each composite. The sum of mobile Pb, Zn and Cu is greatest for the Sunday No.2 followed closely by the May Day composite (table 4). However, table 4 shows 40% of the sum of total Pb, Zn and Cu in the May Day composite is accounted for by the mobile or potentially mobile form of these metals, highest of all the composites. At the concentrations in which these occur, Pb can be considered the most problematic. Ribet et al. 1995 make the case that reductive dissolution of weathered mine tailings by organic covers intended to remediate the tailings may release metals into the environment. They equate the reducible phase of the tailings with the component extracted by 2M hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in 25% (v/v) acetic acid (HOAc), which would encompass the  $\text{Fe}_{\text{am}}$  phase extracted in this study and likely extend into the  $\text{FeOx}_{\text{cryst}}$  phase. The mobilization of metals by action of decaying organic matter in the mine wastes studied here is feasible. Likewise, the mobilization under natural conditions of metals associated with the ion-exchangeable and carbonate phases is feasible.

**Table 4 Total metals ( $\Sigma$ ), metals in mobile phases, and sum of mobile ( $\Sigma$  Mobile) metals in <2mm composites (n.d. means not detected)**

	May Day ( $\mu\text{g/g}$ )	Yukon ( $\mu\text{g/g}$ )	Sunday No.2 ( $\mu\text{g/g}$ )	Venir ( $\mu\text{g/g}$ )
$\Sigma$ Pb	5092	2081	7824	1569
H <sub>2</sub> O-Soluble	22	11	144	44
Ion-Exchangeable	50	10	130	15
Carbonate	320	60	250	60
Amorphous Fe-MnOx	1700	900	2300	300
$\Sigma$ Mobile Pb	2092	981	2824	419
$\Sigma$ Zn	1662	1363	607	228
H <sub>2</sub> O-Soluble	22	33	67	28
Ion-Exchangeable	n.d.	n.d.	n.d.	n.d.
Carbonate	n.d.	n.d.	n.d.	n.d.
Amorphous Fe-MnOx	700	30	40	n.d.
$\Sigma$ Mobile Zn	722	63	107	28
$\Sigma$ Cu	291	1040	305	237
H <sub>2</sub> O-Soluble	1.1	7.8	6.7	78
Ion-Exchangeable	n.d.	n.d.	n.d.	n.d.
Carbonate	n.d.	n.d.	n.d.	n.d.
Amorphous Fe-MnOx	30	22	58	29
$\Sigma$ Mobile Cu	31	30	65	107

#### CONCLUSION

Sequential extractions can be used to determine the mode of occurrence of metals in mine wastes in the sense that with these extractions metals are partitioned into operationally defined phases. The extractability of

metals in each phase varies with particle size, but not necessarily in a systematic manner. The mineralogical composition of the mine wastes influences selection of extraction procedures. Interpretation of extraction results is facilitated to a limited extent by XRD mineralogical analysis. Limitations are due primarily to the lack of specificity of the extraction procedures but also to the relatively high XRD detection limits and the presence of amorphous material in the wastes. The XRD-amorphous material appears to be extracted with the  $\text{FeOx}_{\text{cryst}}$  phase and the residual, or silicate phase. The increasing chemical strength of the steps in sequential extractions provides a means for evaluating the mobility and availability of metals in mine wastes. As a result, sequential extractions may be useful in studies addressing the impact of mining activity on the environment.

#### **ACKNOWLEDGEMENTS**

We thank the property owners and custodians for granting access to the properties, the USGS Mineral Resources Program for supporting this and related investigations, the members of the Mine Waste Characterization project for their help and encouragement, and the reviewers of this paper.

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