

# Batch Investigations on Elemental Dissolution from Copper Mine Tailing Pond, Khetri, India: Evaluation of the Environmental Contamination Potential

Sanghamitra Kundu, Adhiraj Singh Rathore, Agni Pushp and Vishal Singh Chundawat

**Abstract**—The present paper reports elemental dissolution characteristics of tailings (both fresh (CT-1) and weathered (CT-2)) from a tailings pond with poor release control at Khetri Copper Mine, Rajasthan, India. Characterization of the tailings samples were conducted using XRD, FEG-SEM and ICP-AES. The results indicated that both the samples composed mainly of quartz and jarosite along with other crystalline phases and the elemental constituents were Zn, As, Cu, Co, Ni, Cd, Fe, Cr, Mn, Pb, Se, Sr, V, Ti, Al, Ba, Si, Ca and Mg. Concentrations of Al, Cu and V in the tailings exceeded the New Zealand waste acceptance screening criteria for Class A landfills. Batch leaching studies on these tailings indicated very high elemental mobility in organic acid as compared to water or inorganic acid. The extract Ni, Fe, Mn, Al, Ca and Mg concentrations in both the TCLP and ASTM exceeded the maximum allowable drinking water concentrations prescribed by WHO for CT-1. Elemental leaching rate was found to be highest within the first two hours of contact with water. These tests demonstrated that elements release were fairly high from the tailings which accentuates its risk being an environmental hazard..

**Keywords**—Tailings, leaching, elements, TCLP, liquid-to-solid ratio

## I. INTRODUCTION

**T**AILING wastes generated from mining activities consist of an assortment of potentially toxic elements hosted by a variety of minerals present in the ore as well as compounds added during the extraction process and thus possess the potential of being an environmental hazard [1]. The impact of these elements on ecosystems may appear in groundwater, surface water and soil. Common minerals and elements found

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in tailings include Arsenic, Cadmium, Barite, Calcite, Fluorite, Radioactive materials which are toxic in nature. Tailing wastes generated from metal mining and smelting have been found to be the cause of contamination of different spheres of the environment in and around the mine sites and tailing dumps worldwide. In a study conducted by Rodríguez et al. (2009) [2] on tailings and soils around a Pb–Zn mine in Spain, it was suggested that the tailings dumped in the area need to be treated because of excess heavy metal pollution. Another study which aimed to investigate the impact of tailings of an old gold mine at Allaqi Wadi Aswan, Egypt, concluded that the soil and plants near and surrounding the tailing were highly toxic due to heavy metal pollution, and hence unfit for grazing or agriculture [3]. Edinger et al. (2008) [4] noted that shallow marine sediments and fringing coral reefs of the Buyat-Ratototok district of North Sulawesi, Indonesia, recorded silicon, manganese, iron, copper, chromium, cobalt, antimony, thallium, and lead in different concentrations due to sub-marine disposal of tailings from industrial and small-scale gold mining using mercury amalgamation. São Domingos mine, which extends from Spain along the southern region of Portugal, in Baixo Alentejo Province, and is one of the long-term activity mines of the Iberian Pyrite Belt dating back to pre-Roman times have been found to cause significant adverse environment impacts due to acid mine drainage production and mobilization of potentially toxic metals and metalloids in residential areas, agricultural fields, downstreams, and rivers [5], [6].

Environmental pollution, including contamination of sediments, soil, surface and groundwater, vegetation, meiofaunal assemblages, marine algae and of small game animals, resulting from copper works have also been reported by various researchers [7]–[15]. Contamination of the environment with elevated levels of toxic elements persisting near as well as several kilometers distant from the copper processing site or the tailings dump site has been indicated in almost all these studies.

Hence, it is imperative to study the dissolution behavior of these various heavy metals and metalloids in the tailings generated from mineral processing, to predict the long term reactivity of these source materials on the surface, within the

dump, on the soil, and on the groundwater. The most often used approaches to assess this elemental mobility are the laboratory batch extraction tests and column leaching experiments. These studies using synthetic water can simulate the surface leaching of mine wastes to predict the natural weathering actions of the tailings to a considerable extent and thus give us the idea of the extent of environmental pollution hazard these waste dumps pose. The experimental conditions under which the leaching studies are conducted in the laboratory can vary reasonably from the actual environment on field; however, the generated data provides a relatively fair idea of the dissolution characteristics of different materials in the waste.

The objectives of this present work were to evaluate the role of pH and related environmental factors on the mobility of Zn, As, Cu, Co, Ni, Cd, Cr, Pb, Se, Sr, V, Ti, Ba, Fe, Mn, Al, Si, Ca and Mg from mine tailings (both fresh and weathered) collected from the Khetri Copper Complex, Rajasthan (i) using two standard toxicity test procedures TCLP-1311 and ASTM D 3987-85; and (ii) as a function of LS ratio, pH and contact time in batch investigations. The results obtained from the experiments will assist in understanding the release mechanisms and the rates of mobilization of the elements from the tailings in different extreme environmental systems and provide a basis for environmental risk assessment and waste management techniques.

## II. STUDY SITE

Khetri, the region considered for this study, situated in the north eastern part of the state of Rajasthan, India, has been the centre of copper mining activity in the historic past, even long before the first geologist Hackett (1877), examined the region towards the end of the nineteenth century. Extensive activity of the ancient miners in the region is evidenced from the old workings spread all over the belt, slag heaps and dumps of mine wastes near the portals of all the old slopes [16]. Development of the more recent Khetri Copper Complex was started by National Mineral Development Corporation (NMDC) and the project was handed over to Hindustan Copper Ltd. (HCL) in 1967 when HCL was formed. Subsequently, smelting and refining facilities were added. This Khetri Copper Complex is some 8 km away from the older Khetri, connected by road and an aerial ropeway. The complex occupies a lower ground and is partially encircled by mineralized hills, the valley of which also serves as the dump or pond for the tailings generated from copper ore processing (Fig. 1). Approximately about 25,000 tons of such material is generated and dumped in the pond annually [17] and this is being done since the last 47 years till today. Hence the amount of tailings collected till date can be comprehended as no other major utilization or displacement of the generated tailings has been done from the tailings pond so far. As is evident from Fig. 1, the side west of the pond overtaking the hills is uninhabited with undulated and hilly terrain, while the eastern/south eastern side of the pond displays agricultural land and human habitats within a radius

of 3 km. The ground surface elevations of both the western and eastern side of the tailings pond are presented in Fig. 1, from which it is evident that the eastern side is at an elevation lower to that of the tailings pond site. If the aquifer elevation profile is assumed to be similar to the ground surface profile, then it can be inferred that the ground water flow direction occurs towards the eastern side from the tailings dump site. Given this case, and from inferences drawn from previous studies, under favoring conditions, a considerable number and amount of elements can easily be leached out from the mine tailings by the interaction with water in the pond and cause contamination not only of the underlying soil but more specifically surface water from runoff and groundwater, which by virtue of the topography of the study area will ultimately reach the agricultural fields and human habitats. The extent of pollution this groundwater will cause, if it is put to various uses at these downstream locations, can easily be comprehended. Gangal (2003) [18] found phenomenal increase in hardness, conductivity, chloride, sulfate and bicarbonate in the groundwater caused by the copper smelter at Khetri. However, detailed studies pertaining to the estimation of the potential of the mine tailings to contaminate the surrounding soil and groundwater, by elemental leaching, have rarely been done.



Fig. 1 Location of Khetri Tailing impoundment (Source: Google Earth)

## III. MATERIALS AND METHODS

### A. Tailings Sample

The tailings samples were collected from the Khetri Copper Complex tailings pond. The fresh sample (CT-1) was collected just at the slurry outlet to the tailings dump/pond as it was being dumped and its adjacent locations and homogenized and the weathered sample (approximately 20 days old) (CT-2) was collected downstream at the farthest point from the slurry outlet. Both the collected samples were moist and were air dried and stored in airtight plastic containers. The dried samples were already in the form of fine powder, hence no crushing was necessary. The mineralogical composition of the samples were studied using X-ray diffraction (Rigaku MiniFlex II) with Cu-K $\alpha$  (1.54 Å) radiation from BITS Pilani. The elemental composition of the tailings samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) from Sophisticated Analytical Instrument Facility (SAIF), IIT Bombay. Jeol JSM-7600F FEG type scanning electron

microscopy (SEM) system at SAIF, IIT Bombay, was used to examine the morphology of the particles.

Element concentrations in the leachates were determined by ICP-MS (PerkinElmer SCIEX ELAN DRc) using standard techniques from Wadia Institute of Himalayan Geology (WIHG), Dehradun.

#### B. Batch Leaching Tests

The tailings samples were subjected to two standard toxicity leaching test procedures viz. Toxicity Characteristic Leaching Procedure (TCLP; EPA method 1311) [19] to simulate worst case scenario of development of acidic solution acting as extrant within the landfill; and American Society for Testing and Materials Shake Extraction of Solid Waste with Water (ASTM D3987-85) [20] to simulate scenarios where the waste is in contact with solutions having a low buffering capacity such as rainwater. Based on the pH of the tailings in de-ionized water (DI) (CT-1 ~ 8.12 and CT-2 ~ 8.4), extraction fluid #2 was used for TCLP. For the ASTM experiments, DI was used as the extraction fluid. The liquid/solid (LS) ratios for both the above extraction tests were maintained at 20:1. The duration for both the tests was 18 h.

Furthermore, batch extractions using DI was performed on the tailings at LS ratios of 5, 10, 20, 30, 40 and 50 ml/g for 48 h to evaluate the effect of LS ratio on metal and metalloid release. To investigate the effect of contact time on elemental release, static extractions using DI water were done continuously for a period varying from ½ h to 7 h. The other conditions for the extractions were maintained similar to the TCLP. Metal and metalloid release as a function of pH was determined by performing batch studies at acidic pH of 3, 4 and 6 which were maintained by adding HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> to DI, separately. The extractions followed the methodology of the TCLP test, albeit for 48 h duration. From the characterization studies, the tailings were found to comprise of the elements Zn, As, Cu, Co, Ni, Cd, Fe, Cr, Mn, Pb, Se, Sr, V, Ti, Al, Ba, Si, Ca and Mg, which were selected as the target elements for the leaching studies. Even though it was observed that Pb, Cd, Sr, Se occurred in traces, they were considered for the study for their potential toxicity.

All the static extraction tests were conducted in a horizontal oscillatory shaker and were conducted in duplicates. After agitation on the shaker, the mixtures were allowed to settle for 5 min for all the methods, and then the aqueous phase separated by decantation. The pH of the leachates was determined immediately after collection. The leachates were then filtered through a 0.45 mm filter paper by vacuum filtration system, and acidified with nitric acid to pH 2. The sampling bottles were preserved of volume change and evaporation [20]. The preserved leachate samples were then sent for analysis for the determination of leached out element concentrations by ICP-MS from WIHG.

## IV. RESULTS AND DISCUSSIONS

### A. Characteristics of the Tailings

The mineralogical composition, determined by XRD and microscopic analyses, (Fig. 2 (a)) showed predominant occurrence of Fe and Si-bearing minerals as goethite, yoderite, jarosite, iron silicon (FeSi), iron zinc (FeZn<sub>7</sub>), quartz and calcite crystalline phases and minor occurrence of ferric sulphate, chalcopyrite, nickel arsenide (Ni<sub>5</sub>As<sub>2</sub>) and zangoboite (TiFeSi<sub>2</sub>) phases [17]. The weathered sample CT-2 showed a marked predominance of oxide and hydroxide phases of various minerals as amesite, cornubite, pyrochroite in addition to quartz and jarosite (also found in CT-1); and minor occurrence of iron sulphate, titanium nitride and algodonite as per the XRD analysis (Fig. 2 (b)). However, since the ore composition may vary from place to place within the mine itself, so it wouldn't be appropriate to establish any correlation between the mineralogy of the fresh and weathered tailings as they may be from different locations within the same mine.

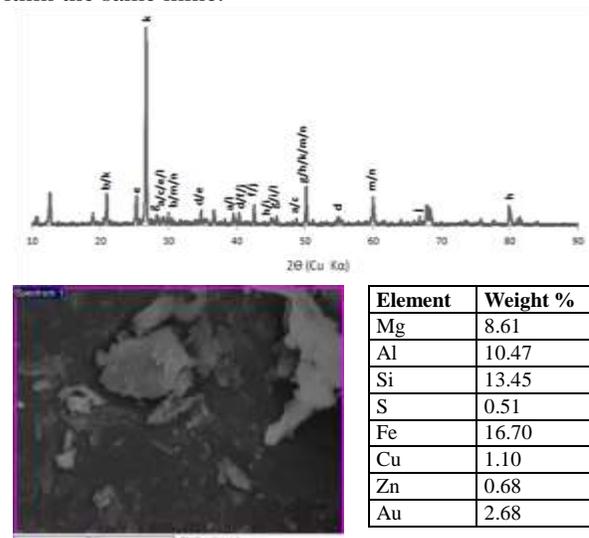
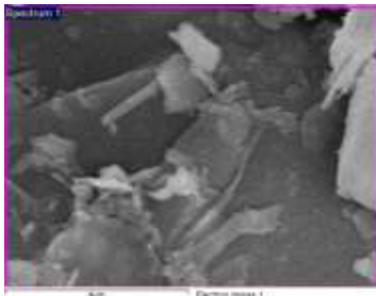
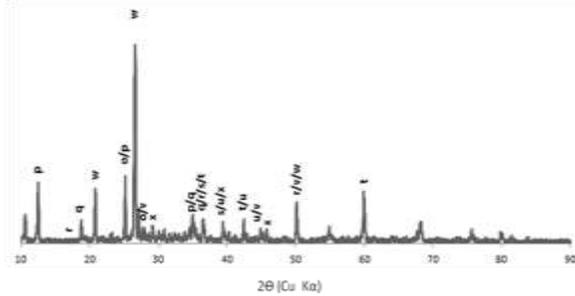


Fig. 2 (a) XRD and SEM-EDS analysis of CT-1: a: Calcite (CaCO<sub>3</sub>); b: Iron Sulphate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>); c: Chalcopyrite (CuFeS<sub>2</sub>); d: Goethite (α-FeO(OH)); e: Yoderite (Mg<sub>2</sub>(Al,Fe<sup>3+</sup>)<sub>6</sub>Si<sub>4</sub>O<sub>18</sub>(OH)<sub>2</sub>); f: Zangoboite (TiFeSi<sub>2</sub>); g: Iron Silicon (FeSi); h: Iron Silicide (FeSi); i: Nickel Arsenide (Ni<sub>5</sub>As<sub>2</sub>); j: Iron Zinc (FeZn<sub>7</sub>); k: Quartz (SiO<sub>2</sub>); l: Jarosite (K(Fe<sup>3+</sup>)<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>); m: Copper Tennantite (Cu<sub>12</sub>As<sub>4</sub>S<sub>13</sub>); n: Copper Iron Arsenic Sulfide ((Cu,Fe)<sub>12</sub>As<sub>4</sub>S<sub>13</sub>)

Elemental analyses using ICP-AES revealed that both CT-1 and CT-2 contained very high concentrations of iron, silica, aluminum, magnesium; relatively high concentrations of copper, calcium, manganese, titanium, zinc; moderate levels of barium, cobalt, chromium, vanadium, nickel, arsenic; and low/trace levels of lead, cadmium, strontium and selenium (Table I). Also as per the New Zealand waste acceptance criteria for landfills [21], the concentrations of Al, Cu and V were found to exceed the screening criteria concentrations for Class A landfills, whereas all the listed elements except Ba were found to exceed the Class B landfill screening criteria. Hence the batch leaching test results presented in the subsequent sections show whether the contaminants are

sufficiently immobilized or not in the waste matrix to understand the threat they pose to the environment.



Element	Weight %
Mg	7.03
Al	7.43
Si	15.96
S	0.58
Cl	0.66
K	5.88
Ti	0.56
Fe	14.27
Cu	1.21
Zn	1.11
Au	2.28

Fig. 2 (b) XRD and SEM-EDS analysis of CT-2: o: Iron Sulphate ( $\text{Fe}_{12}\text{S}_{11}\text{O}_{51}$ ); p: Amesite-2H ( $\text{Mg}_2\text{Al}_2\text{SiO}_5(\text{OH})_4$ ); q: Cornubite ( $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$ ); r: Pyrochroite ( $\text{Mn}(\text{OH})_2$ ); s: Dyscrasite ( $\text{Ag}_3\text{Sb}$ ); t: Titanium Nitride ( $\text{TiN}_{0.9}$ ); u: Algodonite ( $\text{Cu}_6\text{As}$ ); v: Iron Silicon ( $\text{FeSi}$ ); w: Quartz ( $\text{SiO}_2$ ); x: Jarosite ( $\text{K}(\text{Fe}^{3+})_3(\text{OH})_6(\text{SO}_4)_2$ )

TABLE I  
TOTAL CONCENTRATION OF ELEMENTS IN CT-1 AND CT-2

Elements	Concentration (mg/kg) CT-1	Concentration (mg/kg) CT-2	Class A	Class B
			landfills	landfills
			Screening criteria (mg/kg)	Screening criteria (mg/kg)
Iron (Fe)	172500 ± 5500	165500 ± 3700		
Silica (Si)	285400 ± 15,800	286400 ± 13,600		
Aluminum (Al)	23300 ± 6400	22000 ± 7500	800	80
Magnesium (Mg)	20700 ± 6200	13000 ± 5800		
Copper (Cu)	1200 ± 1100	1800 ± 1000	100	10
Calcium (Ca)	6600 ± 910	4200 ± 860		
Manganese (Mn)	2300 ± 400	1900 ± 320		
Titanium (Ti)	5750 ± 1200	4800 ± 1300		
Zinc (Zn)	1100 ± 4300	1800 ± 1300		
Barium (Ba)	60 ± 9	690 ± 120	2000	200
Cobalt (Co)	70 ± 16	50 ± 11		
Chromium (Cr)	60 ± 11	80 ± 12	100	10
Vanadium (V)	60 ± 10	80 ± 13	40	4
Nickel (Ni)	30 ± 5	30 ± 4	200	20
Arsenic (As)	5 ± 1	30 ± 2	100	10

Data reported here is a rounded-off average of 3 replicate analyses for each CT-1 and CT-2

## B. Batch Leaching Tests

### 1) Comparison of TCLP and ASTM Tests

Table II shows the concentration of the leached out elements from the TCLP and ASTM tests along with a check against various standard limiting values, viz: the limit values of waste acceptance for land filling stated in the Annex 2 of the 2003/33/CE Council Decision (based on 1999/31/EC Directive) [22], TCLP regulatory limits and desirable drinking water limit as per World Health Organizations (WHO) standards. As seen from Table II, the leached out concentrations of almost all the elements were higher in TCLP extracts as compared to ASTM method. The increase in elemental mobility may be due to the fact that the elements may have combined with acetic acid (TCLP extraction fluid # 2) to form water soluble organic complexes or elemental solubility may have increased due to reduction of pH [23]. Based on the TCLP extract elemental concentrations, the waste can be deemed as non-hazardous when compared to TCLP regulatory levels as evident from Table II. However, comparison of the leached elemental concentrations of both TCLP and ASTM with regulatory levels of different federal agencies, applying comparable parameters, posed concerns about the pollution potential of the disposed tailings without proper measures. It is worth pointing out that extract concentration of Zn, Cu, Ni and Cr exhibited higher values than inert limit for waste acceptance criteria as per TCLP method for both CT-1 and CT-2, while Zn and Ni showed higher values for the same in the ASTM method for CT-1. Furthermore, it was observed that the TCLP leached Ni, Fe, and Pb concentrations were higher than the WHO recommended values for drinking water for both CT-1 and CT-2 and TCLP leached Cu, Cr concentration exceeded WHO recommended drinking water values in CT-1; the concentrations of Ni and Fe in the ASTM leachates of CT-1 exceeded the maximum allowable concentrations prescribed by WHO and Fe and Pb exceeded the same in the ASTM leachate of CT-2.

### 2) Effect of Liquid-to-Solid (LS) Ratio

Figs. 3 (a) and 3 (b) show the change in the leaching behavior of the elements with the change in the LS ratio from 5 to 50 for both CT-1 and CT-2. With the increase in the LS from 5 to 50, the pH of the extract solutions has been found to drop from 8.7 to 7.3, respectively.

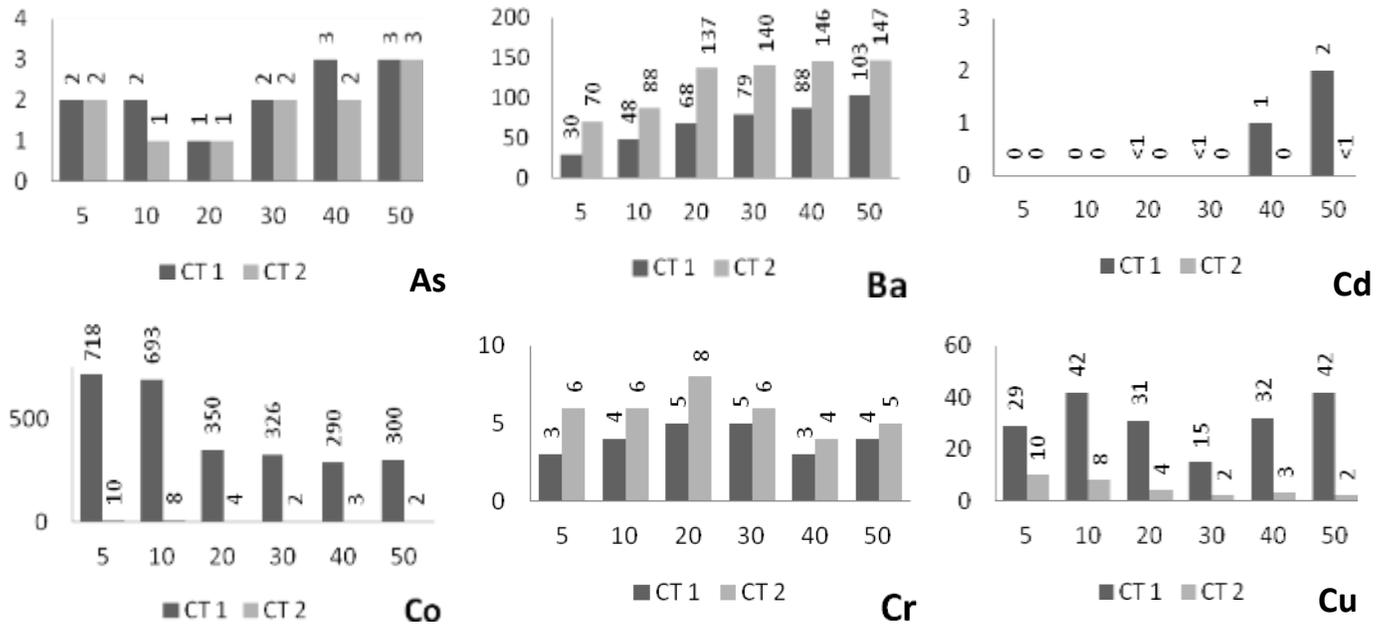
Results indicate that the change in extract elemental concentrations for both CT-1 and CT-2 followed a similar trend with the change in the LS ratio. The leached Ba, Cr and V concentrations in CT-2 were found to be higher when compared to CT-1. This can probably be attributed to the initial high concentrations of the concerned elements in original CT-2 sample as evident in Table I.

TABLE II  
CONCENTRATION OF ELEMENTS IN CT-1 AND CT-2 IN TCLP AND ASTM LEACHATES

Elements	TCLP (mg/kg)		ASTM (mg/kg)		Waste Acceptance Criteria, mg/kg			TCLP (mg/l)		ASTM (mg/l)		Desirable drinking water limit as per WHO (mg/l)	Regulatory level TCLP (mg/l)	
	CT-1	CT-2	CT-1	CT-2	Inert	Non-hazardous	Hazardous	CT-1	CT-2	CT-1	CT-2			
Zn	7.98	12.32	5.34	0.62	4		50	200	0.399	0.615	0.267	0.031	4	
As	0.16	0.02	0.04	0.04	0.5		2	25	0.008	0.001	0.002	0.002	0.01	5
Cu	43.56	5.86	0.74	0.7	2		50	100	2.176	0.293	0.037	0.035	2	
Co	9.26	3.04	7.02	0.06					0.462	0.152	0.351	0.003	-	
Ni	7.92	2.18	4.58	0.18	0.4		10	40	0.396	0.109	0.229	0.009	0.07	
Cd	-	-	-	0	0.04		1	5	< 0.001	< 0.001	< 0.001	0.000	0.003	1
Cr	2.94	0.78	0.1	0.2	0.5		10	70	0.147	0.039	0.005	0.010	0.05	5
Pb	0.38	0.4	0.14	0.22	0.5		10	50	0.019	0.020	0.007	0.011	0.01	5
Se	0.04	0.06	0.02	0.06	0.1		0.5	7	0.002	0.003	0.001	0.003	0.04	1
Sr	4.72	7.66	3.74	6.28					0.236	0.383	0.187	0.314	-	
V	0.06	0.02	0.02	0.06					0.003	0.001	0.001	0.003	-	
Ti	8.04	6.42	6.7	0.56					0.402	0.321	0.335	0.028	-	
Ba	2.78	5.86	1.2	2.66	20		100	300	0.139	0.293	0.060	0.133	0.7	100
Fe	3524	450.4	797.2	28.92					176.2	22.52	39.86	1.446	0.4	
Mn	772.8	453.2	502.4	4.7					38.64	22.66	25.12	0.235	-	
Al	321.04	52.32	14.02	7.86					16.052	2.616	0.701	0.393	-	
Si	312	162	110	96					15.6	8.1	5.5	4.8	-	
Ca	5686	3754	3846	536					284.3	187.7	192.3	26.8	150 – 300	
Mg	2072	1650	1682	330					103.6	82.5	84.1	16.5	150 – 300	

The batch experiments indicate that the extract Ca, Fe, Mg, Mn, Si, Ti concentrations show a marked decrease in the solubility with the increase in the LS ratio. With the increase in LS ratio, the increase in the amount of the liquid phase results in some dilution of the elemental concentration, naturally resulting in decreased extract metal and metalloid concentrations.

Ba, Pb, Sr, Zn showed a noteworthy increase in the leached concentrations with the increase in the LS ratio. For Pb and Zn, this may be ascribed to the fact that there exists a significant relationship of Zn and Pb with Mn in solution which form complex aggregates in solution [24].



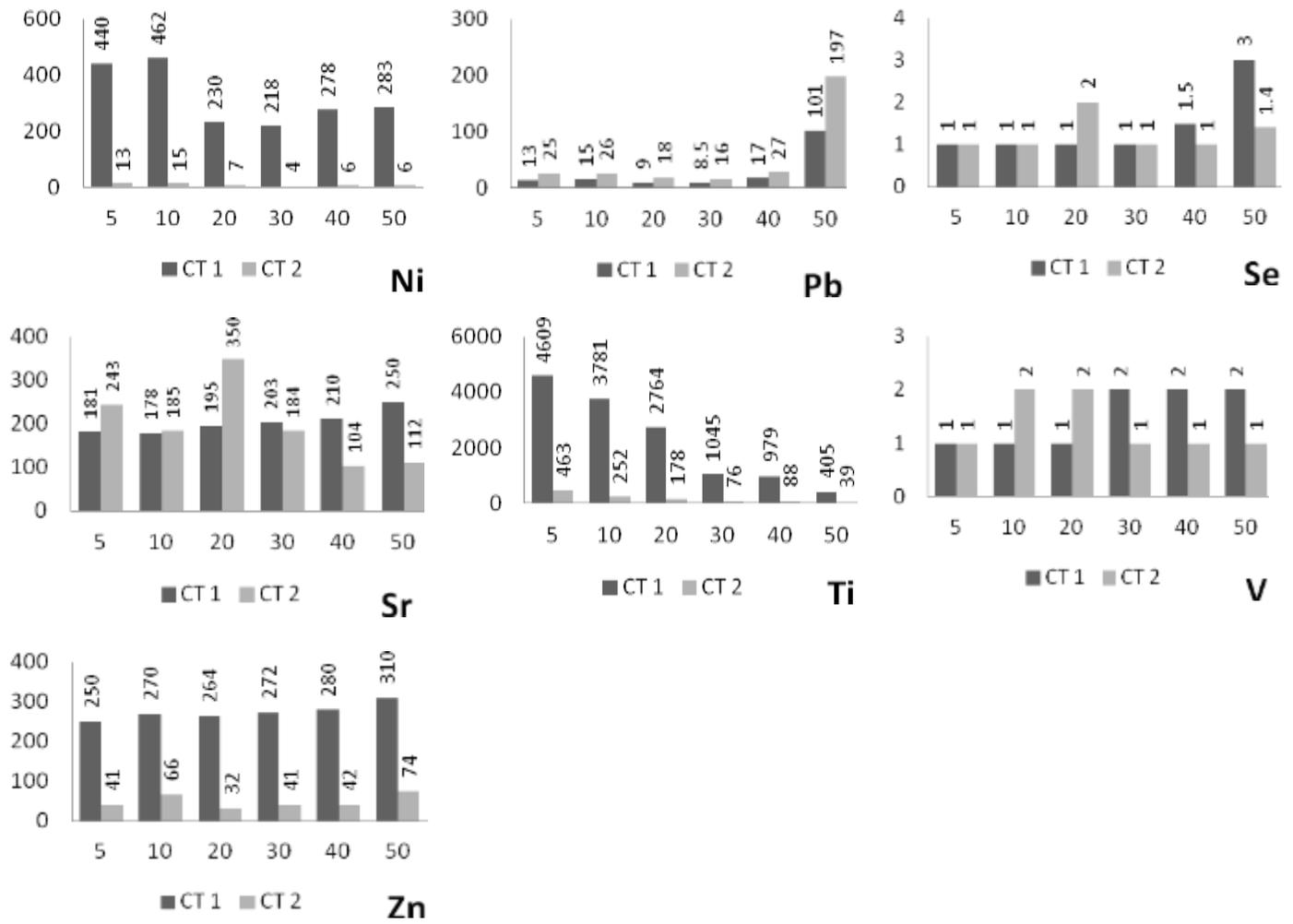


Fig 3 (a) Metal release as a function of LS ratio [x-axis: LS ratio; y-axis: metal release concentrations in µg/l]

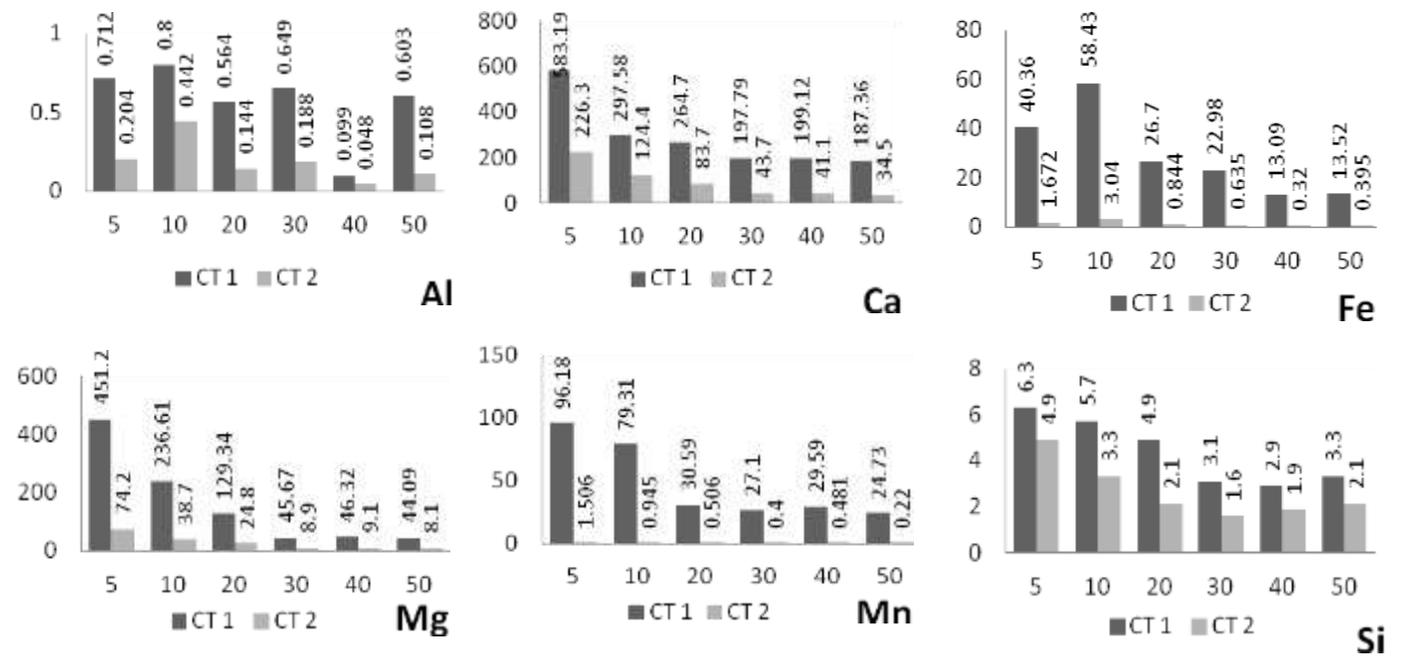


Fig 3 (b) Metal release as a function of LS ratio [x-axis: LS ratio; y-axis: metal release concentrations in mg/l]

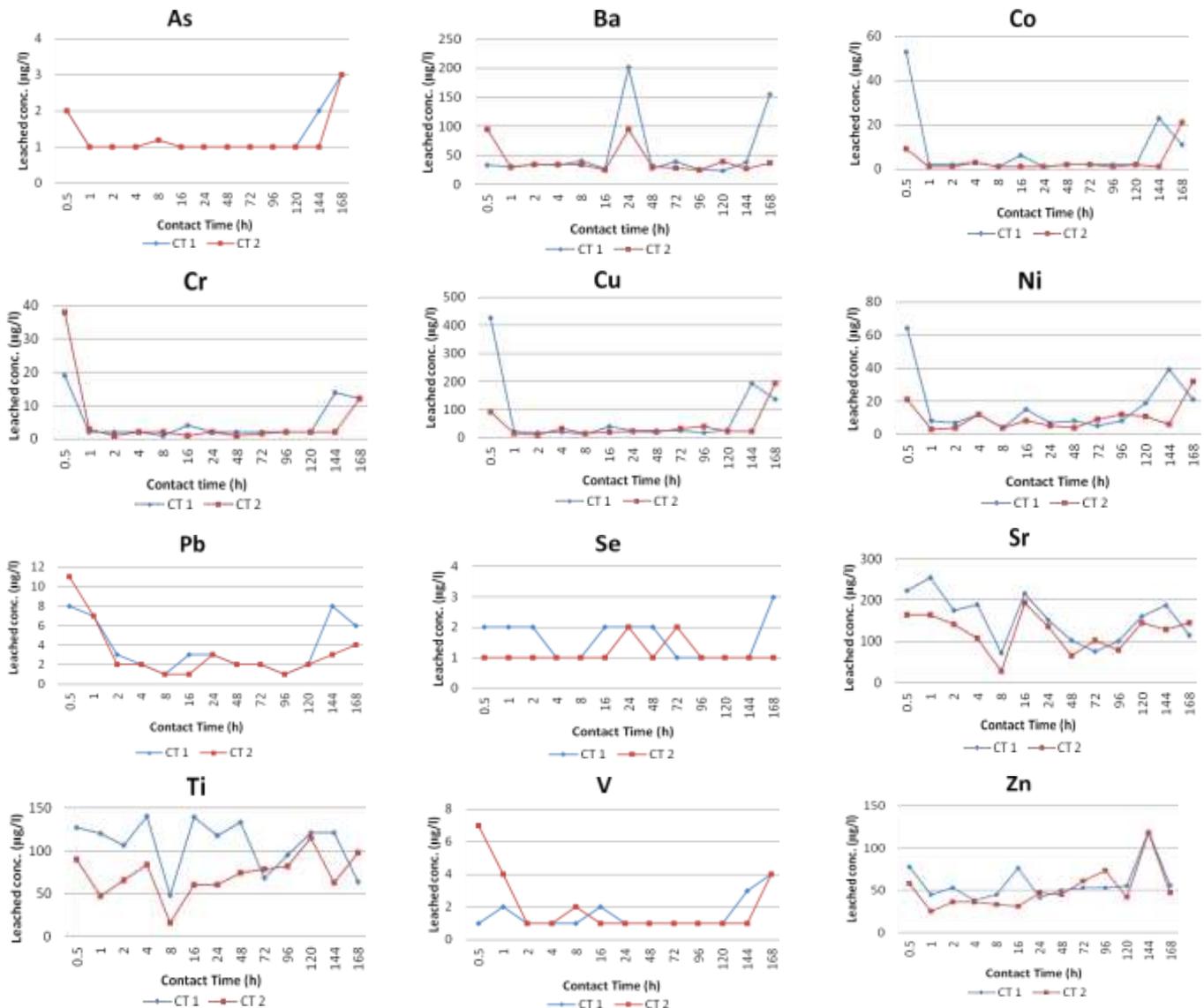
### 3) Effect of Contact Time

Fig. 4 represents the effect of contact time on the leachability of the various elements being considered for the study at a specific LS ratio of 20:1. The results indicate that for almost all elements a sharp drop in the concentration of the leached out elements were observed within the first 2 hours of contact, indicating a very high leaching rate within the initial hours of contact with the extraction fluid for both CT-1 and CT-2. This indicates that a major amount of the element(s) mobilize out within the initial period of contact with the extracting solution (DI in this case) with decrease in leaching rates in the later periods. Moreover, for almost all elements the leached concentrations from CT-2 is found to be less than CT-1 indicating some leaching has already occurred within the 20 days and is still continuing. The elements Sr, Ti, Zn, Ca and Mg, however, show variability in leached

concentrations with time indicating that the leaching of these elements may continue to occur for a longer duration with high concentrations. These fluctuations in elemental concentrations of Sr, Ti, Zn, Ca and Mg may be attributed to time consuming reactions which lead to metals hydrolysis and precipitation processes.

The pH of the samples did not show wide variation for the contact time studied, with the average pH fluctuations ranging within 6.8 – 8.2 for both the samples CT-1 and CT-2.

From Fig. 4, it is also observed that there is a sudden spike in the extract elemental concentration for most of the elements after 120 hours. This may provide an important insight into the fact that the dissolution properties of the elements from the tailings increase with time which may actually cause enrichment of elements into the surrounding soil environment at a much later stage after disposal.



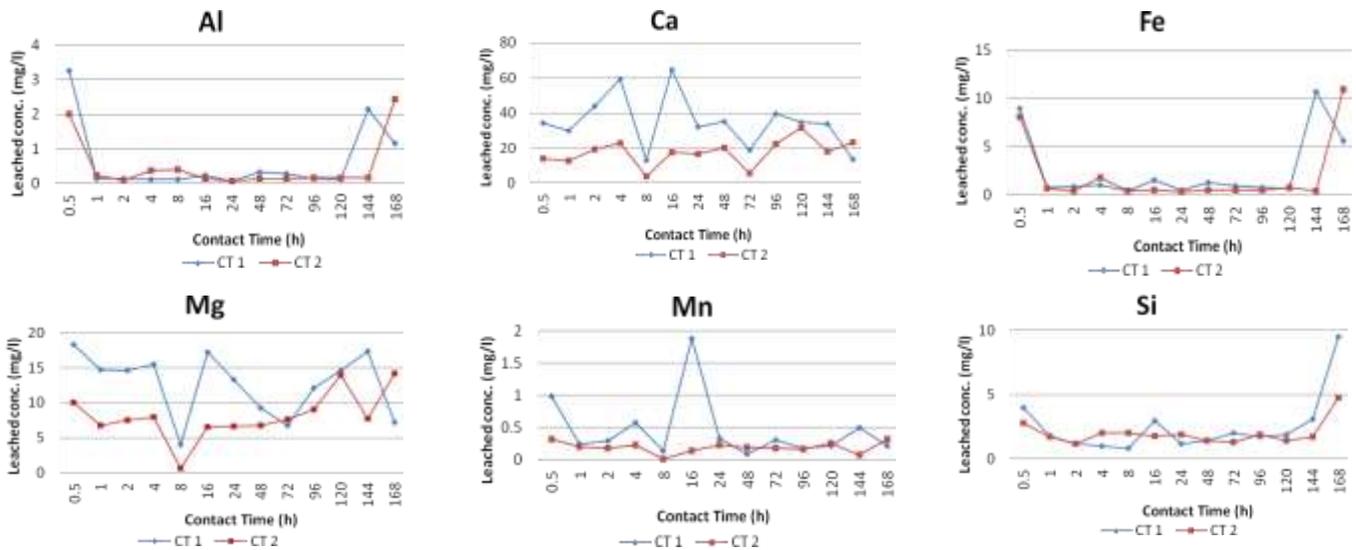


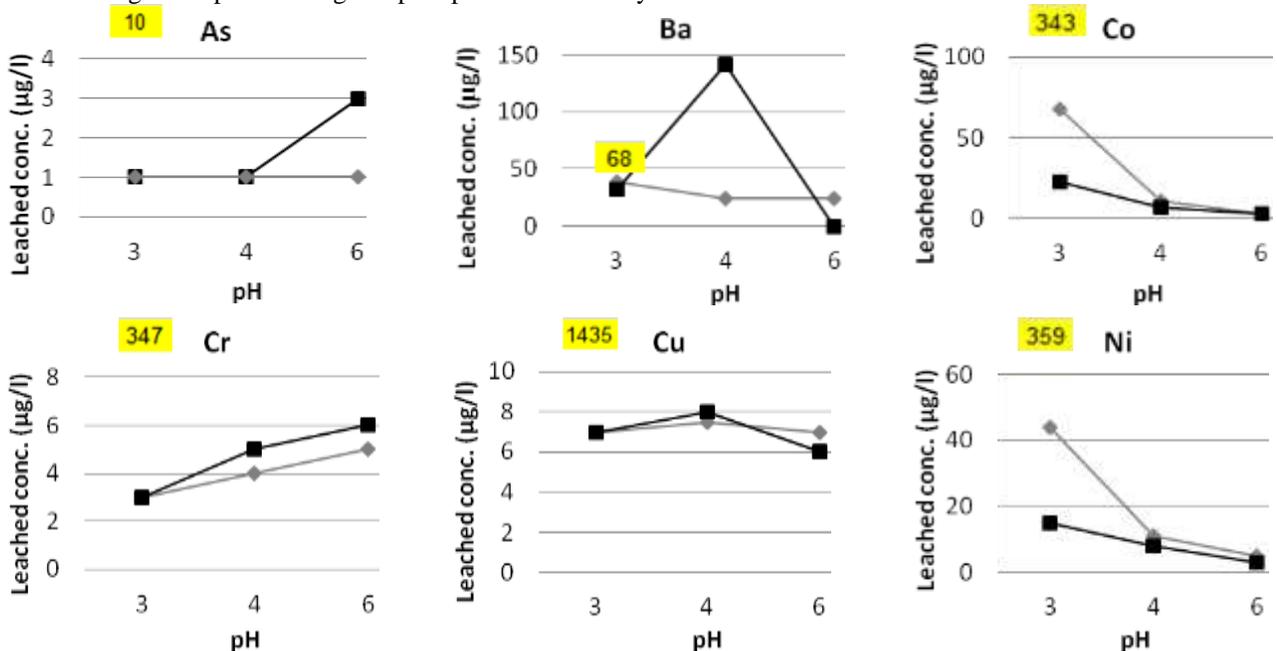
Fig. 4 Variation of elemental concentration with Contact Time

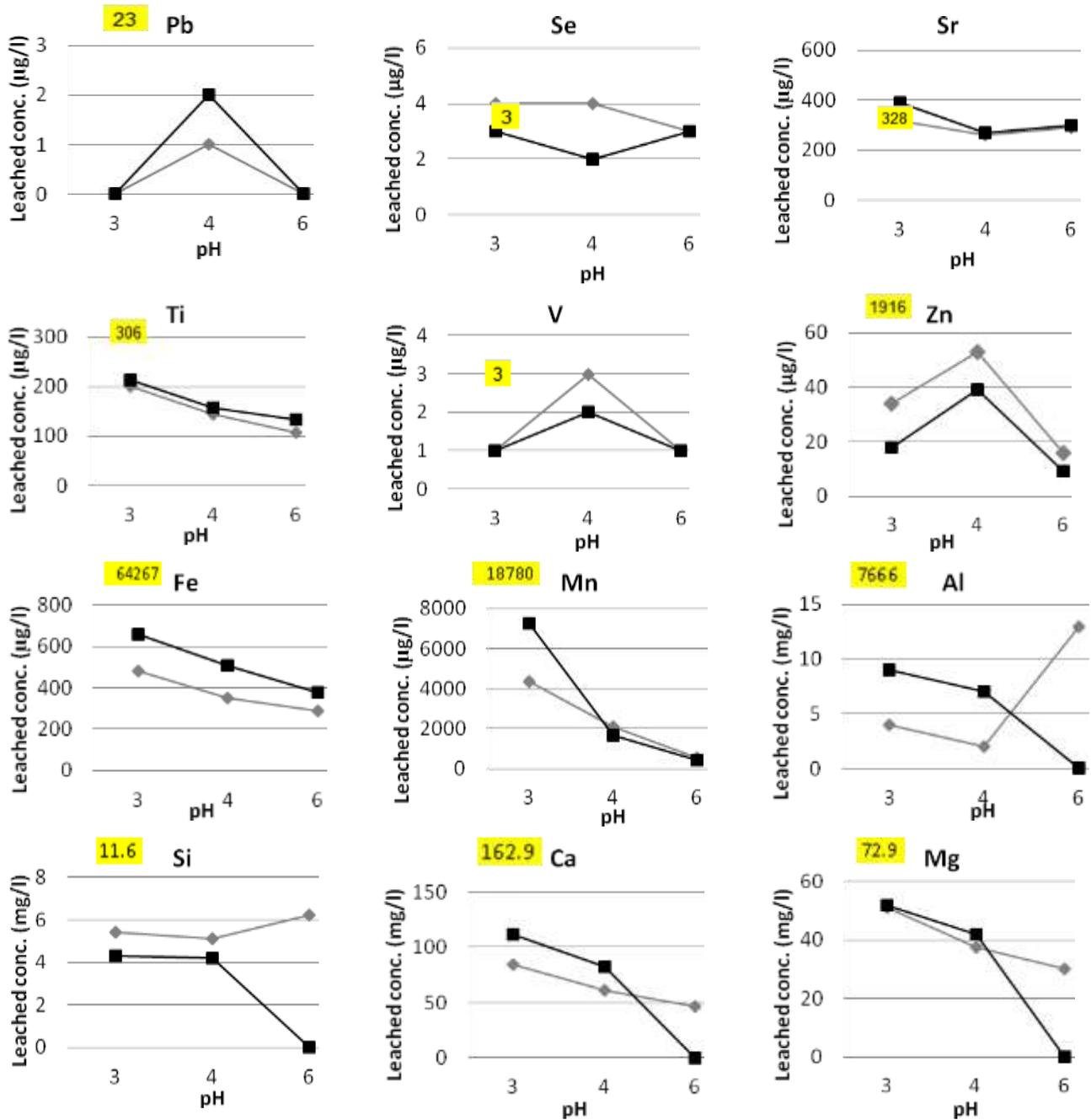
4) Effect of pH

Fig. 5 shows the effect of pH due to inorganic acids  $H_2SO_4$  and  $HNO_3$  on the elemental mobility of CT-1. Barring a few elements, it is clear from the graphs that almost all elements exhibited a decrease in their solubility with increase in the pH. This can also be correlated with the fact that the elemental leaching concentrations in solution at pH 7 with de-ionised water were less as compared to that at lower pHs studied here. There is a great presence of Fe, Al, Si, Mg and Mn in the tailings and often they have been found to control the concentration of the other metals in solution or sediments [24]. Hydrolysis may tend to proceed as the pH rises with the high concentrations of iron, aluminum, silica and magnesium in the tailings sample causing co-precipitation/secondary

precipitation reactions with the formation of insoluble complex ions which in turn may limit the solubility of the elements [25]. The extent of this precipitation is also, however, a function of pH of the solution, the particular metal or metalloid, the concentration of aqueous complexing agent (which creates competition among the element for the formation of complexes) and the concentration of the metals [13].

As evident from the graphs, the extract elemental concentrations using these inorganic acids as leachants were much less compared to that using organic acid (acetic acid in TCLP) as leachant, even though the contact time in the former case was higher due to the formation of soluble organic complexes with acetic acid.





Yellow Boxes on the graph shows leaching with acetic acid at pH 3

Fig. 5 Variation of elemental concentration at pH 3, 4 and 6 brought about by inorganic acids [◆ H<sub>2</sub>SO<sub>4</sub>, ■ HNO<sub>3</sub>]

### V. CONCLUSION

It was observed in the present study, that the concentrations of all the elements listed in CT-1 and CT-2, exceeded the concentrations as per the New Zealand waste acceptance screening criteria of Class B landfills while the elements Al, Cu and V exceeded the screening criteria concentrations for Class A landfills as well. Elemental leaching from Khetri Copper Mine Tailings (CT-1 and CT-2) was investigated under equilibrium batch studies at different experimental conditions. The results suggested that concentration of elements Zn, Cu, Ni and Cr, in the TCLP extracts, were all

higher than the allowed inert limits for solid wastes acceptance criteria imposed by the EC Directive. The concentrations of Zn and Ni in the extract also exceeded the non-hazardous material limit value for both TCLP and ASTM methods and hence need to be very carefully monitored. A comparison of the leached concentrations of the elements with the permissible drinking water limits recommended by WHO also revealed that Ni, Fe, Mn, Al, Ca and Mg exceeded the WHO recommended values in both TCLP and ASTM leachates for CT-1. It was observed that all the elements studied exhibited high leaching in acidic pH

with very high leaching rate in organic acid at a much lower contact time as compared to inorganic acid indicating the probability of formation of soluble organic complexes with ease. Batch data as a function of LS ratio indicated that for Ca, Fe, Mg, Mn, Si and Ti dissolution mechanisms contributed to metal release. The leaching of Ba, Pb, Sr and Zn, increased with increasing LS ratio. The effect of contact time on the leachability of the elements showed more than 50% drop in the leached concentrations, from the start, within 2 hours of contact with the leachant for most of the elements. This can lead us to infer that the maximum mobilization rate of elements will occur during and immediately after rainfall on the tailings impoundment. The elements Sr, Ti, Zn, Ca and Mg did not show any specific leaching trend with contact time.

The results presented in this paper provide information and enlightens us in understanding the mobility of various elements present in the Khetri Copper Mine tailings and also helps us to determine the maximum amount of contaminant that can be leached under extremely harsh conditions. However, care should be taken in interpreting the leachability of the elements as batch tests could significantly overestimate potential release due to negligible mass transfer limitations and absence of other geological and hydrological factors. The study area is a considerably dry region that receives an average annual rainfall of about 450 – 500 mm, which somewhat limits the mobilization of the elements to a certain extent. The geochemical factors affecting the reactions, which can help in determining the speciation of the elements, going on inside the waste dump is also unknown. Moreover, this study considers only the leaching behavior of the tailings without taking into account the potential for cumulative effects of elemental release over longer time durations. Hence, long-term leaching tests are still required to obtain further information about leaching behavior of these elements for making a more adequate assessment and anticipate the changes in release over time.

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