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Identification of the Origin and Behaviour of Arsenic in Mine Waste Dumps Using Correlation Analysis: A Case Study Sarcheshmeh Copper Mine

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Abstract

Knowledge of the probable origin and behaviour of arsenic certainly gives valuable insights into the potential for transfer in the environment and of the risks involved in mining sites. Sequential extraction analyses are common experiments often used to study the origin and behaviour of potentially toxic elements. The method, however, presents some deficiencies, including labor-intensive procedure, interferences of phases, being impractical for testing large number of samples in heterogeneous environment as well as inability for determining the individual minerals as source or sink terms for toxic elements. This study attempts to determine the origin and behaviour of arsenic in waste dump using correlation analysis approach. To this end, sixty samples were collected from two waste dumps at the Sarcheshmeh Copper Mine in Kerman Province, Iran. The statistical results along with previous experimental investigations and also sequential extraction experiment revealed that adsorption on muscovite is the main source, and that oxy hydroxides of iron and manganese are the main adsorbent minerals which control the concentrations of arsenic in the waste dumps of the Sarcheshmeh copper mine.

Keywords: *Acid mine drainage, bioavailability, paste pH experiment, sequential extraction analysis*

1. Introduction

Arsenic (As) is the 20th most abundant element with overall average concentration of approximately 2 mg Kg^{-1} in the earth's crust [1]. Arsenic contamination of soil may be prevalent in association with mining, milling, and smelting of copper, lead, and zinc sulphide ores as well as coal fly ash and agricultural use of arsenical pesticides [2, 3]. Both high (up to 500–10,000 mg Kg^{-1}) and low concentrations of arsenic in soils and sediments are potentially of concern because they may contribute to high concentrations of arsenic in pore or surface waters through desorption or dissolution, in plants through growth and uptake, or in animals (including humans) through ingestion [4]. Chronic exposure to arsenic may result in skin and internal organ cancers, impaired nerve function, kidney and liver damage, or skin lesions [5].

Most risk from arsenic is associated with the forms of arsenic that are easily accessible to the surface water or, in other words, biologically available (bioavailable) to humans and other creatures. Commonly, bioavailability of arsenic has been investigated by sequential extraction analysis wherein the arsenic is categorised into several phases by extracting solutions with greater strength [6]. These phases include soluble in water, exchangeable, reducible, oxidisable, and residual. They are often attributed to the associating elements, bonded or adsorbed on hydroxyl sulphates, exchangeable sites in clay minerals or carbonates, in the iron and manganese oxy hydroxides, organic matter/sulphides, and silicate phases, respectively [7]. According to this classification, there is a reduction in the risk of toxic elements from “water soluble” to “residual” phase [8].

Although sequential extraction analysis has been previously implemented in numerous projects to evaluate potentially toxic elements, it has some shortcomings due to complexity of procedure, interferences of phases, inability in considering heterogeneity in a medium and lack of exact determination of individual mineral as source or sinks terms.

The complexity is related to the wide range of possible processes, which leads to selectivity of different reagents, the extraction time, the solid-to-liquid ratios, the type of agitation, the methods used for liquid/solid separation, the mass of the test sample, and, the rinsing method according to the variety of protocols [9, 10, 11]. Therefore, it will be a difficult task to compare the results obtained by different laboratories using various protocols. Consequently, different quantification errors are associated with sequential extraction analysis, compared with single step extraction namely total extraction such as ICP method [12].

Ideally, extractants are designed to dissolve selectively one mineralogical phase of the initial material, but practically, according to the type of ore body, the other phases are also solved. This phenomenon might lead to interference of phases and result in uncertainty of result [11, 13].

Due to being labour-intensive, the application of sequential extraction is limited to a few number of samples. Waste dumps are huge in volume and have high heterogeneity from mineralogical, physical and geochemical point of view [14]; therefore, the small number of samples may cause misunderstanding about the mechanisms contributing to fate of toxic elements. Furthermore, sequential extraction can only determine the type of minerals containing elements where it is unable to distinguish the individual mineral responsible for immobilisation of toxic elements. For example, sequential extraction can determine nickel as an exchangeable element on clay minerals but cannot determine which mineral adsorbs it.

Given the above-mentioned drawbacks, it is necessary to develop a method to describe the phases of potentially toxic elements, particularly in mine waste dump. To date, no study has attempted to develop a methodology for determining the origin and behaviour of potentially toxic elements substituting sequential extraction test. This subject highlights the bioavailability of them which is very obligatory for environmental risk assessment of waste dumps as a basis of future remediation program. According to previous investigations in Sarcheshmeh mine, arsenic is shown to be a crucial element for environmental impacts associated with stream sediments. Therefore, the main goal of the study was to implement a correlation analysis to develop a general methodology for identifying the origin and behaviour of arsenic at mine waste dump environment. It is expected that the proposed methodology could be applied to other sites with similar characteristics, both in abandoned and active mines producing very heterogeneous wastes.

2. Study area

The Sarcheshmeh porphyry copper deposit is the biggest copper mine in Iran and one of the largest Oligo-Miocene deposits in the world. Sarcheshmeh mine is situated in south of Iran at 30° N, 56° E and about 160 km southwest of Kerman city (Figure 1a). This mine is located in a semi-arid climate with a mean annual precipitation of 440 mm [17].

Open pit mining has been employed for more than 35 years in the Sarcheshmeh area. The mine site consists of mining units, tailings dam, waste dumps, processing, melting and molding plants. The Shour stream (Figure 1b) is a major drainage to which mine water, acidic drainages from waste dumps, pilot and processing plants waste waters and also other industrial contaminated effluents associated with the Sarcheshmeh copper complex discharge.

The Sarcheshmeh ore body, with dimensions of 2000 m by 900 m, contains 1200 million tons of ore with average grades of 1.13% copper and 0.03% molybdenum, 3.9 ppm silver, and 0.11 ppm gold and a cut-off grade of 0.4% copper [18]. Development of mining activities in the region has resulted in over 400 million tons of mining wastes. In order to minimize the transportation costs, the mining wastes are usually dumped in natural valleys near the mine. The mine has 31 active and inactive waste dumps, some of which generate acid mine drainage, especially in the wet seasons.

Drawing on the previous studies at the Sarcheshmeh mine site, dumps No. 19 and 31 (Figure 1b) have high acid-producing potential

(AP) [8, 19]. Based on the modified Sobek method [20], the obtained Net Acid-Producing Potential (NAPP) suggests that these dumps can generate 107 and 92.17 kg H_2SO_4 per ton of waste, respectively [19]. The releasing of arsenic is a consequent of Acid-Producing Potential and AMD generation; therefore, the present study focuses on these two dumps for identifying the fate of them.

3. Materials and methods

3.1. Sampling

To achieve the objective of the study, six trenches (A, B, C, D, E and F) were excavated in the waste dumps No. 19 and 31 from the surface to a depth of 6.5 meters (Figure 1 c, e). A total of sixty samples were taken from the trenches in November 2011. Sampling program comprised two patterns. The first pattern was performed in trenches A, C, E and F vertically (Figure 1 c, d, e, f). In order to perform a geochemical and mineralogical characterization in apparently homogeneous layers, the second pattern consisted of the sampling in layers that inclined at an angle of 38° in trenches B and D (Figure 1 e, f). This angle was the repose slope of the waste materials from the surface to dump toe which composed interbedded layers in the waste dump.

To take representative samples, nearly 4 kg of waste material, sieved by screen 4 mesh, were collected in each sampling location. Samples were taken using a stainless steel

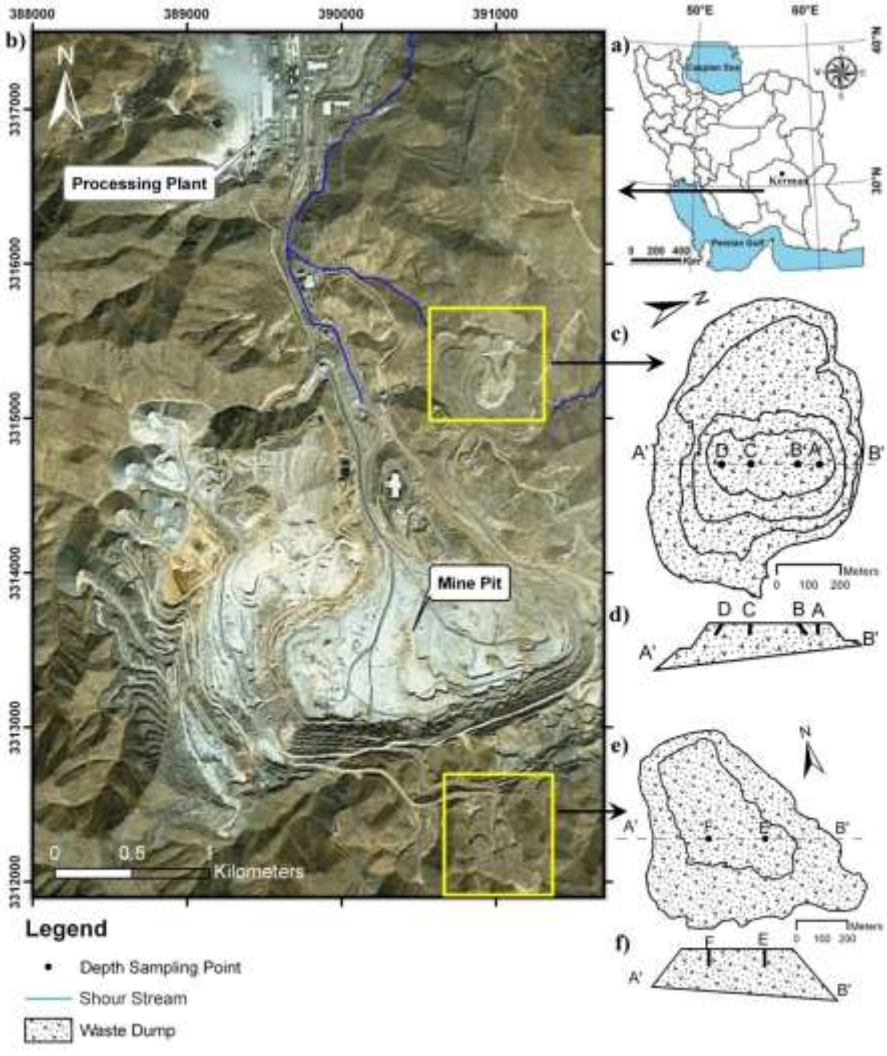

Figure 1. Overview of the Sarcheshmeh mine area a) Geographical situation of Sarcheshmeh mine in Iran b) A plan view of Sarcheshmeh mine complex (modified from [21]) c) Plan of the dump No. 31 accompanied by the location of trenches d) Cross-section of dump No. 31 e) Plan of the dump No. 19 accompanied by the location of trenches f) Cross-section of dump No. 19, Note that the vertical scale of the cross-section is exaggerated for better visibility.

device, and stored in air-tight polyethylene plastic bags. The samples were then sent to the Central Laboratory of the Sarcheshmeh Copper Complex for preparation and performing further processes required before chemical and mineralogical analyses.

3. 2. Analytical method

Total concentration of arsenic was determined using inductively coupled plasma mass spectrometry (ICP-MS) method at the LabWest Minerals Analysis Pty Ltd., Australia. The detection limit for determination of arsenic concentration was 0.01 ppm. Mineralogical studies including quantitative and qualitative analyses of primary and secondary minerals were carried out by X-ray diffraction (XRD) and studying the thin and polished sections of the collected samples. XRD was qualitatively conducted by a Philips Multipurpose X-ray diffraction system at the Iran Mineral Processing Research Centre (IMPRC). Mineralogical quantification was done with Rietveld method [22]. This method can provide quantitative estimations of minerals, even poorly crystallized ones, by having chemical composition of samples such as ICP or X-ray Fluorescence (XRF) data [23].

3. 3. Experiments

3.3.1. ASTM standard test method for determining the form of sulphur

In environmental impact assessment of Acid Mine Drainage (AMD), determination of pyrite and secondary hydroxyl sulphateminerals originated from pyrite oxidation process is very crucial. Due to a high detection limit (approximately 2 percent) and unfavourable efficiency related to poorly crystalline minerals, quantitative XRD cannot exactly determine negligible minerals content such as pyrite, hydroxyl sulphate and iron oxy hydroxide minerals. Therefore, a method introduced by ASTM (D 2492) [24] was employed to determine such minerals. This method was based on two steps which were conducted for all samples.

Step 1: Diluted Hydrochloric acid (HCl) was used to dissolve hydroxyl sulphate and oxy hydroxide minerals. It should be noted that diluted HCl cannot digest sulphide minerals. The obtained solution from this step was diluted to volume and analysed for total iron and sulphate (SO_4^{2-}). Sulphate was measured by Emission Spectrometry which represented the hydroxysulphate minerals content. For convenience sake, sulphate content was transformed into sulphate sulphur concentration (S_s) by stoichiometric calculations. Total iron content of the solution was measured by Atomic Absorption Spectrometer (AAS), which reflects the presence of iron content in hydroxyl sulphate and oxy hydroxide minerals. Hydroxy sulphate minerals have usually low concentrations in waste dumps. However, iron has a low or even no contribution in these minerals. For example, gibbsite, alunite and bluidite contain no iron in their formula but butllerite and jarosite have maximum 27% and 33% of iron, respectively. Thus, it is be reasonable to attribute total iron to iron oxyhydroxide minerals ($Fe_{o\text{-}h}$).

Step 2: Diluted Nitric acid (HNO_3) was added to residue material of step 1 in order to dissolve pyritic sulphur. Assuming that all iron content is in pyritic form, pyrite content was stoichiometrically calculated from the iron concentration. For uniformity, pyrite content was transformed into pyritic sulphur concentration (S_{py}).

3. 3. 2. Paste pH

Paste pH is a simple and inexpensive method to primarily estimate the presence of reactive carbonate or readily available acidity [25]. It was determined by weighing 50g of prepared sample and adding 50mL of distilled water. After mixing for 5s, the slurry was left to stand for 10 min. The electrode was, then, inserted into the slurry and after swirling slightly, the pH was measured until a stable value was obtained. To save space, the paste pH is called p.pH in the following.

3.3.3. Sequential Extraction test

The selectivity of reagents for sequential extraction test has been a focus of criticism because a wide range of possible secondary phases are associated with waste dumps materials in sulphide deposits [13]. After reviewing sequential extraction schemes, particularly those adapted to the specific mineralogy of porphyry Cu-sulphide ores, and evaluating the advantages and limitations of each protocol and reagents that were used for each phase, a 9-step fractionation procedure was selected. This procedure was well performed by Khorasanipour *et al.* [26, 27] in soil and sediment environment around Sarcheshmeh mine. In this procedure, elements are separate into nine geochemical phases: water soluble, exchangeable, carbonates, amorphous iron oxy hydroxides, crystalline iron oxides, manganese oxides, organic matter (oxidisable), primary sulphide and residuals.

The Khorasanipour *et al*. procedure is listed in Table 1.

Table 1. Sequential extractions procedure applied by Khorasanipour *et al*. [26, 27] in Sarcheshmeh mine.

phases	procedure
water soluble	1 g sample into 50 ml deionized H_2O, shake for 1 h, at RT
exchangeable	50 ml, 1 M, NH_4-acetate pH 7 shake for 2 h, at RT
carbonates	50 ml, 1 M, Na-acetate or Acetic acid pH 5 shake for 2 h
amorphous Fe oxy hydroxides	50 ml, 0.2 M NH_4-oxalate pH 3.0 shake for 1 h in darkness, at RT
crystalline Fe oxides	50 ml, 0.2 M NH_4-oxalate pH 3.0 heat in water bath 80 °C for 2 h
Mn oxides	50 ml, 0.1 M NH_2OH–HCl pH 2 shake for 2 h
organic matter	50 ml, 35% H_2O_2 pH 2 heat in water bath 85 °C for 1 h
primary sulphide	Combination of $KClO_3$ and HCl, followed by 4 M HNO_3 boiling
residuals	HNO_3, HF, $HClO_4$, HCl digestion

RT: Room Temperature h: hour

In this study, the sequential extraction test was conducted to validate the proposed method. Therefore, regarding the result of the method, only the exchangeable phase was partitioned. Therefore, 1 g of air dried sample (<80 µm) was treated with 50 ml of ammonium acetate 1 M at pH 7 under stirring for 2 h at room temperature. Then, the suspension was centrifuged at 2500 rpm for 30 min, and the supernatant was filtered through a 0.45 µm filter. Finally, the obtained solution was analyzed by ICP for arsenic.

3. 4. Statistical analysis

To perform a proper geochemical characterization of arsenic at the waste dumps, a correlation analysis was conducted using Pearson's correlation coefficients. It describes the interaction or the level of linear association among pairs of variables that helps better understand pollution signatures in industrial areas [28]. In this method, the data are treated, and then interpreted into groups according to degree of correlation coefficients. These groups describe any trends or significant similarity between various variables.

To form the correlation matrix, the minerals with source and sink roles for arsenic were selected as the variables. Arsenopyrite, orpiment and realgar are the primary minerals containing arsenic [29].Yet, studying the polished sections of the samples revealed the absence of the above minerals in the waste dumps of Sarcheshmeh. In addition, a small amount of arsenic may be present in the structure of coexisting pyrite [29].

As such, Spy which is representative for pyrite content was used in correlation analysis. The most common adsorbents of toxic elements include the carbonates, organic matter, clay, iron and manganese oxy hydroxide and hydroxyl sulphate minerals [2, 30, 31]. All these adsorbents were detected in the Sarcheshmeh waste dumps, except for carbonates and organic matter. Therefore, the correlation analyses was established between arsenic and observed minerals with source and sink behaviour. After data collection, correlation analysis was performed using SPSS software version 16.0.

4. Result and discussion

4.1. Mineralogical and geochemical analyses

Primary minerals observed in the studied waste dumps as well as their descriptive statistical characterizations are tabulated in Table 2.

For all of the materials, the main minerals found by the XRD analysis were quartz and muscovite which were present in all samples. Pyrite, illite, kaolinite, orthose, albite, chlorite, montmorillonite and epidote were also present in some samples. The carbonate content, as the most major neutralising agent, was zero in all samples. The XRD data and polished sections study also indicated that the main sulphide mineral was pyrite accompanied by small amounts of chalcopyrite and magnetite.

At the Sarcheshmeh waste dumps, several secondary minerals were detected by XRD in some depths (Table 3). Moreover, amorphous iron oxy hydroxide minerals were visually observed in waste dumps, which were not detected by XRD as they were negligible and had low level of crystallinity. Therefore, they were measured in term of ($Fe_{o\text{-}h}$) by ASTM standard test method.

The concentrations of arsenic accompanied by paste pH and ASTM standard test results are given in Table 4. In this table, arsenic concentrations are presented for each trench (A, B, C, D, E and F) from surface to bottom of each trench. The name of each sample point contains DS-(trench name) (number of sample in the trench) that DS is the abbreviation of Depth Sampling.

As shown in Table 4, there are no pronounced trends of arsenic variation, pH value and ASTM results with depth. This phenomenon is due to heterogeneity of material from physical and geochemical aspects which lead to occurrence of different mechanisms related to AMD generation. The separation of these mechanisms is very essential for investigating the origin and geochemical fate of arsenic.

Table 2. Descriptive statistics of primary minerals in the studied waste dumps (All variables are in term of wt %).

mineral	quartz	pyrite	muscovite	illite	kaolinite	orthose	albite	chlorite	montmorillonite	epidote
Number	60	48	60	56	19	29	48	48	11	5
Minimum	24	2	5	4	4	5	5	5	4	4
Maximum	53	20	23	11	9	9	46	28	15	8
Mean	40.08	6.65	12.57	7.13	6.15	7.28	14.69	11.90	6.36	6.02
Std. D	6.68	4.19	3.43	1.40	1.19	1.13	9.25	6.59	3.64	1.58

Table 3. Descriptive statistics of secondary minerals in the studied waste dumps (All variables are in term of wt %.).

mineral	butlerite	jarosite	gypsum	carfosiderite	bluidite	alunite
Number	12	12	11	1	1	2
Minimum	5	5	5	6	7	3
Maximum	9	9	9	6	7	5
Mean	6.42	6.83	6.17	6	7	4
Std. D	1.16	1.47	1.03	-	-	1.41

Table 4. Chemical properties of the samples collected from paste pH, ICP and ASTM data.

Sample	Depth (m)	paste pH	ICP (mg Kg^{-1})	ASTM (%)		
			As	S_s	S_{py}	Fe_{o-h}
DS-A1	0.2	3.92	86.5	0.74	10.74	3.72
DS-A2	0.5	2.43	32.8	1.54	3.49	3.86
DS-A3	0.8	3.16	40.5	1.83	7.47	3.40
DS-A4	1.1	3.30	31.1	3.22	3.70	4.43
DS-A5	1.5	4.36	13.2	7.06	8.41	2.38
DS-A6	2	3.79	10.5	0.85	0.34	2.71
DS-A7	2.5	3.86	14.4	0.75	1.49	2.55
DS-A8	3	4.04	4.7	0.50	0.20	1.70
DS-B1	0.2	3.13	12	1.50	1.19	3.23
DS-B2	0.5	5.93	65	0.16	1.20	4.84
DS-B3	0.8	6.19	112	0.22	1.30	4.83
DS-B4	1.1	6.26	131	0.26	1.19	5.99
DS-B5	1.5	6.40	134	0.21	1.30	4.67
DS-B6	2	6.26	123	0.28	1.71	5.01
DS-B7	2.5	6.00	55	0.27	1.49	5.67
DS-B8	3	6.06	191	0.26	1.43	7.02
DS-B12	5	2.88	23.5	2.34	0.80	4.84
DS-C1	0.2	6.00	45	0.26	1.46	4.31
DS-C2	0.5	6.34	64.9	0.20	1.33	4.30
DS-C3	0.8	5.97	35.1	0.21	1.13	3.83
DS-C4	1.1	6.00	66.3	0.23	1.70	5.36
DS-C5	1.5	5.99	63.5	0.24	1.55	5.33
DS-C6	2	6.21	49	0.17	1.32	3.99
DS-C7	2.5	6.08	133	0.25	1.31	7.81
DS-C8	3	6.30	90.2	0.37	1.46	9.31
DS-C9	3.5	6.38	22.2	0.21	0.91	4.57
DS-C10	4	6.38	70	0.37	1.35	8.47
DS-C11	4.5	6.40	74.5	0.43	1.65	6.88
DS-C12	5	5.99	45.6	0.47	1.37	6.42

Sample	Depth (m)	paste pH	ICP (mg Kg^{-1})	ASTM (%)		
			As	S_s	S_{py}	Fe_{o-h}
DS-D4	1.1	4.24	11.1	0.52	1.43	3.78
DS-D5	1.5	5.40	48	0.51	1.87	4.38
DS-D6	2	5.68	18.6	0.47	1.57	4.21
DS-D7	2.5	6.30	28.1	0.33	1.58	4.09
DS-D8	3	3.99	11	1.08	0.75	4.17
DS-E1	0.2	3.84	19.4	1.47	3.05	6.01
DS-E2	0.5	5.97	99	0.55	1.23	7.93
DS-E3	0.8	4.57	23.5	0.49	1.48	4.87
DS-E4	1.1	6.01	36.7	0.49	0.78	6.46
DS-E5	1.5	6.68	28.3	0.48	0.69	6.73
DS-E7	2.5	5.61	45.9	0.31	1.23	6.05
DS-E8	3	6.20	14.7	0.42	3.98	3.21
DS-E9	3.5	6.34	38.6	0.87	6.10	4.19
DS-E10	4	6.37	15.4	0.36	5.48	2.89
DS-E11	4.5	6.39	15.4	0.63	4.82	3.15
DS-E12	5	4.19	7.6	0.57	5.23	3.06
DS-E13	5.5	4.42	24.5	0.56	5.67	3.13
DS-E14	6	4.13	23.5	0.47	6.05	2.33
DS-E15	6.5	6.17	28.4	0.39	6.50	2.46
DS-F1	0.2	2.94	26	1.66	5.80	3.00
DS-F2	0.5	3.75	36.4	0.36	7.31	1.90
DS-F3	0.8	3.72	10.6	0.66	6.67	2.13
DS-F4	1.1	3.84	156	0.45	0.15	2.19
DS-F5	1.5	3.88	177	0.45	0.23	2.96
DS-F7	2.5	3.63	169	0.90	0.20	3.39
DS-F9	3.5	6.19	39.3	0.37	0.14	7.42
DS-F10	4	5.75	85	0.37	0.16	7.32
DS-F11	4.5	4.36	53.5	0.51	0.13	5.83
DS-F12	5	4.17	58.3	0.77	0.18	6.10
DS-F13	5.5	4.90	43.2	0.45	0.13	5.08
DS-F14	6	4.17	37.4	0.48	0.21	6.77

S_s: sulphate sulphur; S_{py}: Pyritic sulphur; Fe_{o-h}: Iron in oxy hydroxide minerals

Table 5. Correlation matrix for all data.

As									
0.33	Fe_{o-h}								
0.42	0.68	Mn							
-0.27	-0.18	-0.45	S_s						
-0.29	-0.48	-0.32	0.23	S_{py}					
0.46	-0.02	0.06	-0.24	0.04	Ms				
0.14	-0.07	-0.02	-0.01	0.12	0.52	Ill			
0.17	-0.05	-0.02	0.17	-0.05	0.32	0.29	Kln		
-0.29	-0.31	-0.43	-0.03	0.51	0.15	0.05	-0.15	Chl	
-0.05	0.16	-0.07	0.15	-0.06	-0.23	-0.14	-0.06	-0.18	Mnt

Fe_{o-h}: Iron in oxyhydroxide minerals; S_s: Sulphate sulphur; S_{py}: Pyritic sulphur; Ms: Muscovite; Ill: Illite; Kln: Kaolinite; Chl: Chlorite; Mnt: Montmorillonite

4. 2. Correlation analysis

So far, only few countries such as USA, Spain and Italy have established a specific legislation for threshold of toxic elements concentrations in different media. According to Spain legislation for arsenic, the concentration of maximum allowable, obligatory investigation and necessary treatment for industrial areas are 20, 50 and 300 ppm, respectively [32]. Arsenic values in the Sarcheshmeh waste dumps samples range from 4.7 to 191 ppm (Table 4). Evidently, it exceeds the maximum allowable and obligatory investigation thresholds. Therefore, there is a great call to identify the sources.

To identify the origin and geochemical behaviour of arsenic, the magnitude of clay minerals, iron in oxyhydroxide minerals (Fe_{o-h}), manganese and pyritic sulphur (S_{py}), and sulphate sulphur (S_s) were added to arsenic concentrations and then correlation coefficients were calculated. Table 5 gives the correlation coefficient matrix. According to the results, there are insignificant correlation coefficients between arsenic and other variables. The results suggest that the correlation matrix (Table 5) is not effective to identify the origin and behaviour of arsenic with this data structure. This may be due to interference of different geochemical conditions caused by weathering and relevant geochemical processes such as release, mobility and adsorption of arsenic. To solve the problem, it might be reasonable to classify the data based on a criterion which can limit the geochemical processes that affect the fate of arsenic. It is expected that the pH is the suitable criterion for separation of geochemical processes. .Thus, the data were categorised based on the p.pH experiment, resulting in four classes and, then, the correlation matrix was calculated for each class, separately. The p.pH classes included (2 < p.pH < 4), (4 < p.pH < 5), (5 < p.pH < 6) and (6 < p.pH < 7).

Correlation values between arsenic and the variables at different p.pHs classes are provided in Table 6. According Table 6, at p.pH between 2 and 4, arsenic indicates a strong correlation (r = 0.84) with muscovite. Although a poorly positive correlation exists between arsenic and muscovite (r = 0.46) for all samples (Table 5), it cannot be reliably interpreted. Therefore, when the data are classified the relationship becomes obvious. For p.pHs between 4 and 5, the correlation coefficient between arsenic and muscovite decreases slightly (r = 0.57). Simultaneously, arsenic shows a strong correlation (r = 0.82) with iron oxy hydroxide minerals (Fe_{o-h}). Therefore, in this p.pH range, it can be inferred that arsenic is present in two forms of adsorbed on the muscovite and iron oxy hydroxide minerals. At p.pH range between 5 and 6, arsenic shows a weak correlation (r = 0.23) with muscovite and a strong correlation (r = 0.78) with Fe_{o-h}. Therefore, one can assume that iron oxy hydroxide adsorbs arsenic at this p.pH range. Finally, the significant correlation (r = 0.69) between arsenic and manganese at p.pHs between 6 and 7 suggests that arsenic was fixed by manganese oxyhydroxide mineral.

As given in Table 6, the hydroxyl sulphate minerals, pyrite, illite, kaolinite, chlorite and montmorillonite do not play any role as a source or sink term for arsenic in Sarcheshmeh waste dumps at any p.pH ranges.

Table 6. Correlation values between arsenic and selected variables at different p.pHs.

p.pH	Fe_{o-h}	Mn	S_s	S_{py}	Ms	Ill	Kln	Chl	Mnt
At all p.pHs	0.33	0.42	-0.27	-0.29	0.46	0.14	0.17	-0.29	0.05
2< p.pH <4	-0.21	-0.57	-0.39	-0.23	**0.84**	0.24	0.22	-0.02	-0.19
4< p.pH <5	**0.82**	0.21	0.16	-0.35	**0.57**	-0.07	0.07	-0.18	0.02
5< p.pH <6	**0.78**	0.27	0.09	-0.43	0.23	-0.22	0.05	0.21	0.13
6< p.pH <7	0.46	**0.69**	-0.46	-0.41	-0.22	-0.27	0.10	-0.57	0.00

The significant correlation are highlighted

Fe_{o-h}: Iron in oxy hydroxide minerals; S_s: Sulphate sulphur; S_{py}: Pyritic sulphur; Ms: Muscovite; Ill: Illite; Kln: Kaolinite; Chl: Chlorite; Mnt: Montmorillonite

4.3. Validation of the proposed method

The capability of muscovite to adsorb arsenic was well documented by Chakraborty *et al.* [33]. They found that muscovite could adsorb arsenic, while the hydrothermal fluid is flowing through the alteration zone at pH between 3 and 8. Therefore, muscovite appears to be the main origin of releasing arsenic in Sarcheshmeh mine. As discussed earlier, the correlation between arsenic and muscovite decreased with an increase in the p.pH. It happened most probably due to the nature of arsenic that tends to transport by increasing pH of the environment [29] and adsorb on the surface of iron and manganese oxy hydroxides at higher p.pH values. Adsorbtion of arsenic by iron and manganese oxyhydroxide minerals are consistent well with the results obtained applying sequential extraction in the Sarcheshmeh mine [8, 17].

Therfore, a scenario can be presented for origin and behaivor of aresenic in Sarcheshmeh waste dumps as follows.Muscovite is considered as a major source of arsenic which is origineted from the hydrothermal fluids related to the time of ore body formation. Rainfall infiltration into the waste dumps increases the pH of pore water. With the pH on the rise, arsenic is leached from the muscovite surface and migrates toward the surface of iron and then toward manganese oxyhydroxides.

Due to the importance of origin-finding of arsenic, it was tried to validate the result of the proposed method usingsequential extraction experiment. As mentioned in section 3.3.3 adsorption on the clay minerals such as muscovite (Exchangeable phase) was revealed on the second step of procedure (see [26, 27]). Therfore, this step was carried out ontwo samples (DS-E1 and DS-F5) which hadp.pH between 2 and 4. The samples contained 19.4 and 177 mg Kg^{-1}of arsenic, respectively (Table 4). The sequential extraction result showed that sample DS-E1 contained 15.8 mg Kg^{-1} arsenic as exchangeable phase, indicating that 81% of arsenic originated from this phase. The similar result was obtained for DS-F5. In this sample, 156 mg Kg^{-1} arsenic leached from the exchangeable phase, suggesting that 88% of arsenic existed in this phase. Therefore, it can be concluded that the results are fully accordant with the origin of arsenic identified by the proposed method.

5. Conclusions

In this study, it was shown that the use of statistical approach as correlation analysis provides a valuable knowledge about the origin and geochemical behaviour of arsenic in the waste dumps of Sarcheshmeh Copper Complex. This method employed the arsenic content together with the exact mineral contents which were classified according to the paste pH experiments. The methodology considered in this study proved to be simple, fast and more exact than the sequential extraction analysis.

The results show that there are a source and two sinks minerals that controlled arsenic concentrations at the Sarcheshmeh waste dumps. As such, adsorption on muscovite surface was the source of arsenic which originated from the hydrothermal fluid relevant to the formation age of alteration zone. In addition, Sink term minerals for control of arsenic were iron and manganese oxy hydroxides. Therefore, the bioavailability of arsenic directly depended on the stability of the corresponding minerals. Consequently, from an environmental point of view, in samples of low paste pH values, muscovite can be responsible for releasing arsenic into environment, especially after rainfall.

The findings in this study can be useful in other mines of the Iranian Copper Belt including Meiduk and Sungun, where similar waste materials can be found. The methodology used may also be applied as a base to characterize other mine sites with huge amounts of waste rocks for developing future prevention and remediation strategies.

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