Study of Aluminum, Copper and Molybdenum Pollution in Groundwater Sources Surrounding (Miduk) Shahr-E- Babak Copper Complex Tailings Dam

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***Abstract*—**Interpolated contour maps drawn for aluminum, copper and molybdenum in downstream monitoring boreholes of water dam in Miduk Copper Complex and the values of pH, redox potential (Eh) and distance from water dam indicate different trends of variation and behavior of these three elements in downward groundwater resources. As these maps exhibit, aluminum is dominant in the most alkaline (pH = 9-11) borehole (MB5) to water dam. The highest concentration of molybdenum is found in the nearest borehole (MB6) to water dam. Main concentration of copper is observed in the most oxidized borehole (MB3 with Eh=293.2mV). The spatial difference among sampling stations can be attributed to the existence of faults and diaclases in the geologic structure of Miduk region which causes the groundwater sampling sites to be impressed by different contamination sources (toe seepage and upper seepage water originated from different zones of tailings dump).

***Keywords*—**Contour maps, Monitoring borehole, Toe seepage, Upper seepage.

I. Introduction

POTENTIAL toxic metals frequently contain a high percentage of inorganic industrial contaminants. Mineral extraction, processing and production activities can cause these kinds of elements to enter the environment in a transformed shape and increase their concentration from a harmless level to a toxic one [4].Ore processing or milling refers to the processing of ore rock to create the size of the desired product, remove unwanted constituents and concentrate or otherwise improve the quality of the desired product [10]. Most of the ore extracted at hardrock mines ultimately becomes mill tailings [6]. Tailings generally leave the mill as slurry consisting of 40% to 70% liquid and 30% to 60% fine grained solids [10]. Whereas a high percent of the slurry is water, some special equipment such as thickeners are designed to deposit the solid phase of the tailings and return water to the production process in concentrator plant. In this case, the ratio between solid and liquid phase of the slurry will be reversed. The slurry is then lead to be stored by the tailings dam. Modern tailings impoundment design often includes low permeability clays or synthetic liners and also engineered caps to eliminate or minimize the leachate escaping from impoundment [10]. Nevertheless, seepage from tailings impoundment is often unavoidable, so the infiltration of seepage water to the adjacent surface and groundwater systems can be counted as one of the main pollution transferring mechanisms from the tailings dumps into the downward groundwater resources [2]. In this condition, the trace elements content of water systems can be changed.The concentration of trace elements is controlled by aqueous complexation and sorption onto particulates [7]. This can be itself obtained as a result of variation in redox potential (Eh), pH, cation exchange, evaporation-attenuation and the existence of microorganisms in aqueous environment [5]. The variation of these factors can partially attributed to temporal changes and partially to spatial ones. Some of these factors can be changed in different zones of tailings dump too. Blowes and Ptacek (1994) and others have shown that typical tailings and waste rock piles (fig. 1) consist of various zones named [15]:

(1) A vadose zone at the top section of the pile, which is the zone of sulfide oxidation and acid generation,
(2) A capillary zone below the vadose zone and just above the water table, which is a zone of acid neutralization and chemical precipitation,
(3) A saturated zone below the water table, which is the zone of attenuation and dissolution,
(4) A zone of transport of dissolved species at the toe of the pile and in ground water beneath the pile.

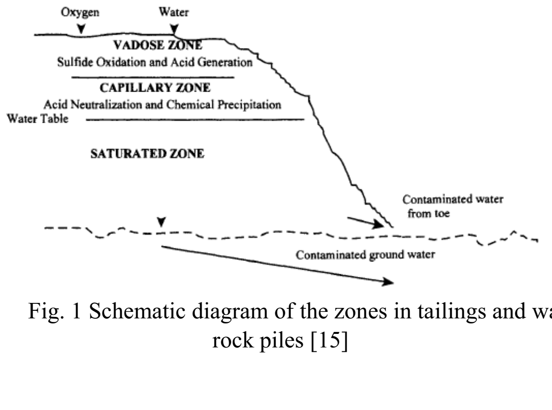

Fig. 1 Schematic diagram of the zones in tailings and waste rock piles [15]

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This kind of structure of the tailings impoundment certainly affects on the seepage water quality and indirectly the downward water systems characteristics. According to the called zones for the tailings dump, we can classify the seepage water into two types named upper seepage and toe seepage. The first major seepage (upper seepage) is originated from the area just below the tailings surface and the other from the toe of the dam, several meters down from the tailings surface. These types of seepage water have variant quality as a result of various source materials or reactions in different parts of the tailings impoundment [13].

activators and modifiers are used in floating unit. The main reactant added to ore mine in floating unit of concentration plant of Miduk Copper Complex is lime ($Ca(OH)_2$). This reactant plays the role of the depressant of the present pyrite (FeS_2) in chalcopyrite. The presence of lime in the tailings of concentrator plant of Miduk Copper Complex increases pH to 10.5-11.5. Only few metals are soluble in downstream water systems under such conditions.

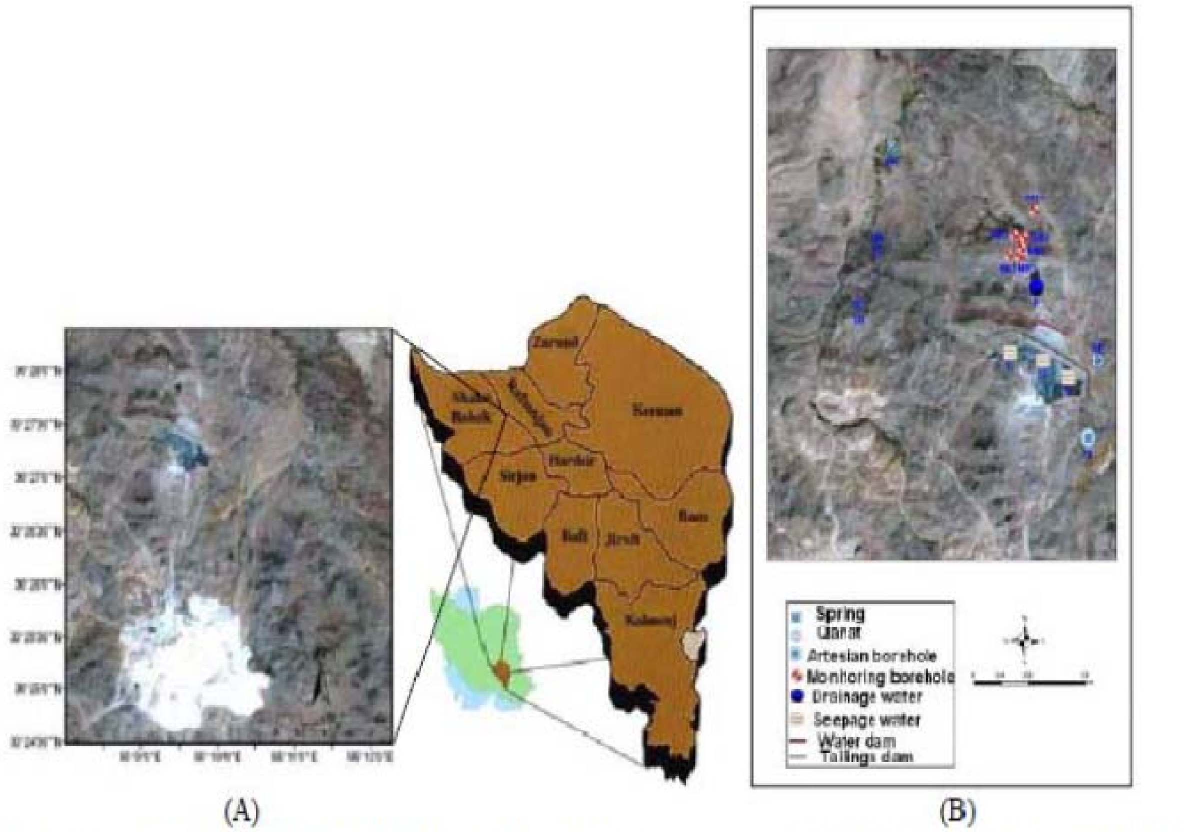

Fig.2 (a) Location of (Miduk) Shahr-e- Babak Copper Complex in Kerman province, and Fig.2 (b) Location of water sampling points.

II. Materials and procedures

A. Site Description

Miduk Copper Complex is located 42km northeast of Shahr-e- Babak city and 132km northwest of Sarcheshmeh copper mine in Kerman province. It is situated between 30° 25′N and 55° 10′E (Fig. 2 (a)). This complex consists of mining units, concentrator plant (processing plant), and retentive structures (tailings and water dams). Two main activities including crushing ore mine and separating valuable minerals from tailings by floatation are carried out in concentrator plant. Main added materials to ore mine are used in floating unit for separating valuable minerals. Five primary reactants consisting of collectors, frothers, depressants,

B. Water Sampling

Six monitoring boreholes (MB1 to MB6) were drilled up to at least 10m below water table. According to water table and maximum depth of groundwater and for chemical analysis and distinguishing the water quality for drinking and agriculture, sampling of 4-5 determined depths was executed. Moreover, sampling of other groundwater resources such as Arghavan village spring (AR) and qanats of Kam Sefid (KM) and Sar Takht (SR) villages as the closest villages to the dam and Latamanu spring (NP) that directly receives leakage of tailings dam was carried out. In addition, four samples were collected from the tailings seepage water with various intervals to tailings dam (samples T1-T3 and D). CB was the sample collected from artesian borehole that is located near the dam. Totally, forty-two water samples were taken from fifteen stations. Location of the sampling points is exhibited in Fig. 2 (b).

C. Water Sampling Equipments and Determination of Element Concentration

KLL-S model of groundwater sampling system (made in German) was utilized for sampling from monitoring boreholes. Polyethylene containers (250ml) were used for transferring samples to the laboratory. Each sampling container was washed three times with the target water before sampling and three sub samples were collected from each station.

The three sub samples were collected for checking precision of the analysis results by calculation of Relative Standard Deviation (RSD). By passing samples through 0.45µ filter paper and decreasing their pH below 2 by concentrated nitric acid (65%), the samples were prepared in (Miduk) Shahr-e Babak Copper Complex laboratory for cation measuring. The water samples were sent to LabWest laboratory (Australia) for determining element concentrations by using inductively coupled plasma mass spectrometry (ICP-MS) method. In order for investigating spatial variations of the elements concentration in downstream groundwater samples (monitoring boreholes), interpolated contour maps were designed in Surfer software.

III. Results and Discussion

A. Descriptive Statistics

In order to determine the accuracy of measurement for concentration of elements, the value of RSD was calculated. By dividing standard deviation to average of the data, RSD value is obtained based on percentage. The averages of RSD values for the measured data including aluminum, copper, and molybdenum (in current study) are respectively (±7%), (±1%), and (±8%).

TABLE I
DESCRIPTIVE STATISTICS OF THE STYDU ELEMENTS IN WATER SAMPLES ON THE BASIS OF µg/L.

Element	Minimum	Maximum	Average	Standard Deviation	Variation Coefficient	Local Background	Drinking Water Standard	Irrigation Water Standard
Al	80.00	1000.00	469.44	214.25	0.45	40.89	200.00	5000.00
Cu	0.05	545.30	44.26	84.25	1.90	24.72	2000.00	200.00
Mo	0.70	1175.30	178.91	353.13	1.97	12.16	70.00	10.00

Descriptive statistics of the study elements, local background values and standards for drinking water (WHO) and irrigation water (FAO) for water samples are given in Table 1 on the basis of µg/L. The order of the concentration average for the study elements is as follows: Al > Mo > Cu. Molybdenum shows enrichment to local background, drinking water and irrigation water standards. On the other hand, Aluminum represents enrichment to local background and drinking water standard. However, copper only indicates enrichment to local background.

B. Interpolated Contour Maps

Different trends of the three above-mentioned elements are observed in interpolated contour maps (Fig. 3) at the sampling depths in monitoring boreholes. Artesian borehole and boreholes MB2, MB5, and MB4 show high concentration of aluminum while respectively MB3 and MB6 represent high concentrations of copper and molybdenum. In order for more detailed investigation on this matter, values of pH, redox potential (Eh) and the measured concentrations for the elements are shown in Table II.

C. Aluminum

According to XRD results of the Miduk tailings samples refered to in Kargar's study [9], about 70% of the tailing combination has been allocated to aluminosilicates. In this case, the tailings seepage water and also the downstream groundwater would be definitely affected by the presence of Al. Considering the concentration of Al in table 2 exhibited the enrichment of all samples in comparison to background value. This result was confirmed by Robertson et al. [16] and Heikkinen et al. [13] who, as it was mentioned before, have

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introduced the tailings mineralogy as a momentous factor impressing the combination of tailings seepage water. By the way, as table 2 indicates, samples collected from boreholes MB2, MB5, MB4 and CB show higher concentration of Al in comparison to others. This can be justified by the highest alkaline conditions in MB2, MB5 and MB4 (respectively the averages of pH in these boreholes are 9.66, 11.24 and 8.04). On the other hand, borehole CB (artesian borehole close to tailings dam) has the most redox potential (the average of Eh is -225mV) among the boreholes. Aluminum is soluble in such conditions. The reason for that these stations indicate various conditions like higher alkalinity or reducible conditions can be related to the effect of the toe seepage on them. According to Heikkinen et al. [13], the toe seepage receives waters mainly along a longer flow path than the upper seepage, through the water-saturated sulphide tailings with a low stage of mineral weathering. The less acidic pH in the toe seepage suggests higher buffering capacity along the flow path of the toe seepage than that of the upper seepage.

TABLE II
CONCENTRATIONS OF ELEMENTS, pH AND REDUCTION POTENTIAL OF WATER SAMPL IN SAMPLING STATIONS

Stations	Depths (m)	Al	Cu	Mo	pH	Eh
MB-16	6	400.00	9.10	33.10	7.20	253.00
MB-110	10	170.00	9.70	33.40	8.10	255.00
MB-114	14	250.00	15.60	33.80	8.10	253.00
MB-116	16	420.00	32.20	35.20	7.90	257.00
MB-28	8	450.00	6.80	7.30	9.50	192.00
MB-212	12	490.00	15.90	7.70	9.50	185.00
Mb-216	16	710.00	17.70	7.90	10.30	190.00
MB-220	20	520.00	7.00	17.00	9.60	215.00
MB-224	24	510.00	10.40	18.30	9.40	218.00
MB-32	2	340.00	64.80	4.40	7.90	325.00
MB-36	6	200.00	27.80	4.20	8.00	300.00
MB-310	10	350.00	59.40	5.10	8.00	303.00
MB-314	14	130.00	545.30	4.00	8.40	274.00
MB-318	18	160.00	94.80	4.40	8.30	264.00
MB-46	6	270.00	17.90	6.10	9.80	216.00
MB-410	10	410.00	9.00	8.30	11.50	153.00
MB-414	14	530.00	9.40	9.60	11.70	180.00
MB-418	18	660.00	7.90	8.50	11.60	170.00
MB-422	22	470.00	10.40	8.80	11.60	190.00
MB-517	17	640.00	13.10	20.00	8.20	108.00
MB-521	21	800.00	12.50	20.10	8.00	145.00
MB-525	25	680.00	28.30	19.20	8.00	190.00
MB-527	27	1000.00	24.20	20.60	8.00	210.00
MB-529	29	790.00	21.90	19.70	8.00	212.00
MB-68	8	140.00	13.10	3.20	7.50	276.00
MB-612	12	330.00	10.00	4.00	7.30	260.00
MB-616	16	400.00	5.90	4.00	7.30	237.00
MB-620	20	430.00	11.50	5.10	7.40	132.00
MB-624	24	710.00	8.70	154.60	7.30	190.00
CB-226	26	720.00	2.30	3.80	7.70	-230.00
CB-230	30	340.00	0.05	0.70	7.70	-220.00
CB-234	34	470.00	0.50	0.80	7.80	-265.00
CB-238	38	860.00	12.40	8.10	7.70	-180.00
CB-242	42	690.00	0.20	2.70	7.70	-230.00
AR	-	523.33	17.16	4.56	8.40	237.00
KM	-	563.33	13.70	2.46	7.90	227.00
NP	-	176.66	45.83	9.30	8.40	258.00
SR	-	513.33	28.80	3.10	7.70	239.00
D	-	156.66	29.93	445.36	8.00	120.00
T3	-	549.33	134.16	640.30	9.90	110.00
T4	-	634.33	190.10	1096.53	9.30	110.00
T5	-	479.00	17.53	1076.23	8.20	115.00

D.Copper

Borehole MB3 that has the highest concentration of copper is known as the most oxidized station (the average of Eh is 293.2mV). Oxidant condition is appropriate for copper solution. Copper has a very high affinity for organic matter and sulfide minerals and is more strongly bound than other trace elements [3], [1], [8]. Copper bound to sulfide minerals will be released in a soluble form under strongly oxidizing condition [11]. On the other hand, metals such as Cu tend to desorb at near-neutral or higher pH values due to increased competition from complexing agents such as aqueous carbonates, which help to keep the elements in solution [7]. Therefore, the high oxidant condition and the pH value (approximately 8 standard units) of MB3 lead Cu to show to highest concentration in comparison to other sampling stations. According Heikkinen and Ra¨isa¨nen [12], who observed that some Cu had been released from sulphide minerals in the shallow sulphide tailings, but not from the sulphides in the saturated layers of the tailings considering the toe seepage characteristics mentioned before, Cu can be originated from the upper seepage of the tailings.

B.Molybdenum

Borehole MB6 is the nearest borehole to water dam and some parts of tailing seepage water enter directly into it. As far as the tailings seepage water samples represent high concentration of molybdenum, the highest molybdenum content in borehole MB6 could relate to its closeness to water dam. The conditions of the solubility of Mo will be readily provided by the hydrolysis of carbonate minerals. This formed an upward trend for Mo concentration by increasing the depth of the tailings dump [14]. In this way, we could dedicate that the possible source of the Mo presence in downstream tailings dam groundwater was the toe seepage.

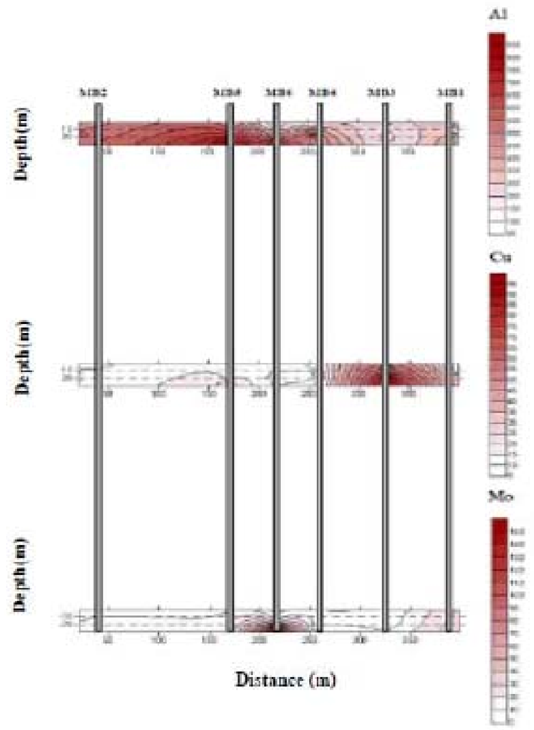

Fig. 3 Interpolated contour maps for Al, Cu and Mo

IV. CONCLUSION

Special tailings dump structure causes the pore water leaked from the deeper zones such as capillary or saturated zones of the dump to have different characteristic in comparison to the surface seepage. These various properties of toe seepage like redox ambient or high alkalinity caused Al and Mo to be dissolved and MB2, MB4, MB5 and CB to be affected by these metals. The reversed conditions such as oxidant and lower pH value of the upper seepage led Cu to be dissolved and MB3, as the most oxidant borehole, to be affected more than other sampling points.

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