

# The leachability of heavy metals from bauxite mine waste

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## Abstract

Pollution caused by tailing dam is one of the most important mining industry issues which creates many environmental problems. Among these, heavy metals play a major role in the destruction and degradation of natural habitats and have harmful effects on human health. In first part of this paper, the effective parameters which leach heavy metals from solid waste of bauxite mine have been investigated. The leaching tank test results indicated that among heavy elements vanadium has the highest concentration at pH of 2, temperature of 60°C, residence time of 8 hours, and the ratio of solid phase to liquid phase of approximately 1. The column leaching tests showed that the increase of the input from 0.4 to 0.9 cc at pH of 7, increased vanadium dissolution. Similarly, after increasing column leaching time from 3 to 30 days, the vanadium dissolution will be 2.5 times. When the pH increases from 7 to 13 caused two times dissolution.

## key words

Mine tailing

leachability

vanadium

Tank leaching

Column leaching

Activated

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## 1. Introduction

One of the main problems of mineral processing industry is landfilling and dumping of mining waste. In general, we can say that mineral waste varies with other waste industry for three reasons;

1. Minerals wastes are not usually weathered; so, they have non-oxidized minerals which may after being oxidized create acidic water of mine.

2. Mineral wastes do not contain organic materials; therefore, they do not have nutrients that are usually found in the soil and are needed for plant growth.

3. Tailings may have high concentrations of heavy metals and reagents added to their grinding and flotation in which case they are potential sources of pollutants.

Contamination related to heavy metals and damp locations are the most important pollution that processing factories produce and tailings dams are the most important points for releasing heavy metals. In this study, it was focused on heavy metals pollution of tailing dam in bauxite processing Factory of Jajarm.

### 1.1 Heavy metals

Heavy metals are some of the most dangerous elements in nature which are very harmful to hu-

man health and the environment. Some of the most common of these metals are Lead, Cadmium, Mercury, Arsenic, etc. These metals were produced by human activities and other factors and slowly get into water and soil around plants and industrial workshops. These metals have high density, high toxicity and are non-decomposed. Table 1 shows the health risks caused by heavy metals.

#### 1.1.1 Effects of heavy metals on plants

Heavy metals such as cadmium, lead and other are among unnecessary elements for plants. If more than the normal amount of them in plants is existed then, will cause negative effects on the adsorption and transfer of essential nutrients in the plant and affect the metabolism and growth of plants [1]. The germination and growth rate of barley is reducing when it is contaminated with cadmium and its density and time of confrontation. Tests showed that germination and growth rate reduced to 45% [2]. The bean seedlings got brown and then died due to cadmium existence [3]. The effects of heavy metals on plants vary in different levels. In the early stages, blocks plant photosynthesis and rice growth and proliferation are reduced which causes disorder in distribution and transfer of plant nutrients [4]. Root life is affected by heavy metals. Shu et al. (1997) studied the root

Table 1: The Health dangers of heavy metals

Element Name	Harmful Effects
Cadmium	Accumulate in the kidneys, the development of heart disease and high blood pressure, bone pain, diarrhea, cancer
Barium	High blood pressure, heart muscle stimulation, seizures, neurological damage, cancer, kidney failure
Mercury	Accumulates in the liver and kidneys, causing toxicity in the brain, impaired nerve to death
Chrome	Pulmonary edema, skin allergy
Copper	Anemia in children, discomfort-the liver, nausea and vomiting.
Lead	Bone pain, nausea and vomiting, paralysis, brain disorders
Arsenic	Skin and lung cancer, weight loss, diarrhea, swelling of body
Nickel	Lung cancer, body swelling
Cobalt	The thyroid factor and blood pressure
Tin and vanadium	Create complications in the larynx, nose and throat



quality in the waste of minerals. The existence of heavy metals (such as lead, zinc, copper and cadmium) prevents the adsorption of nutrients and minerals and affects the plant growth significantly [5]. The permissible levels of heavy metals in water resources offered by various organizations (tabulated in Table 1) bring about a sample for domestic livestock and poultry drinking. Researchers have been proposed several ways to remove heavy

metals from solutions; they were mentioned in Table 2.

### 1.2 Tailing Dam of Jajarm Alumina Factory

Jajarm Bauxite Factory is sited at 5 km northeast of city of Jajarm which is located at southeast of North Khorasan province (Figure 1). Bayer aluminum extraction process is being practiced in this facility. The factory produces over a million ton of red mud, annually. Factory tailing dam is ring type

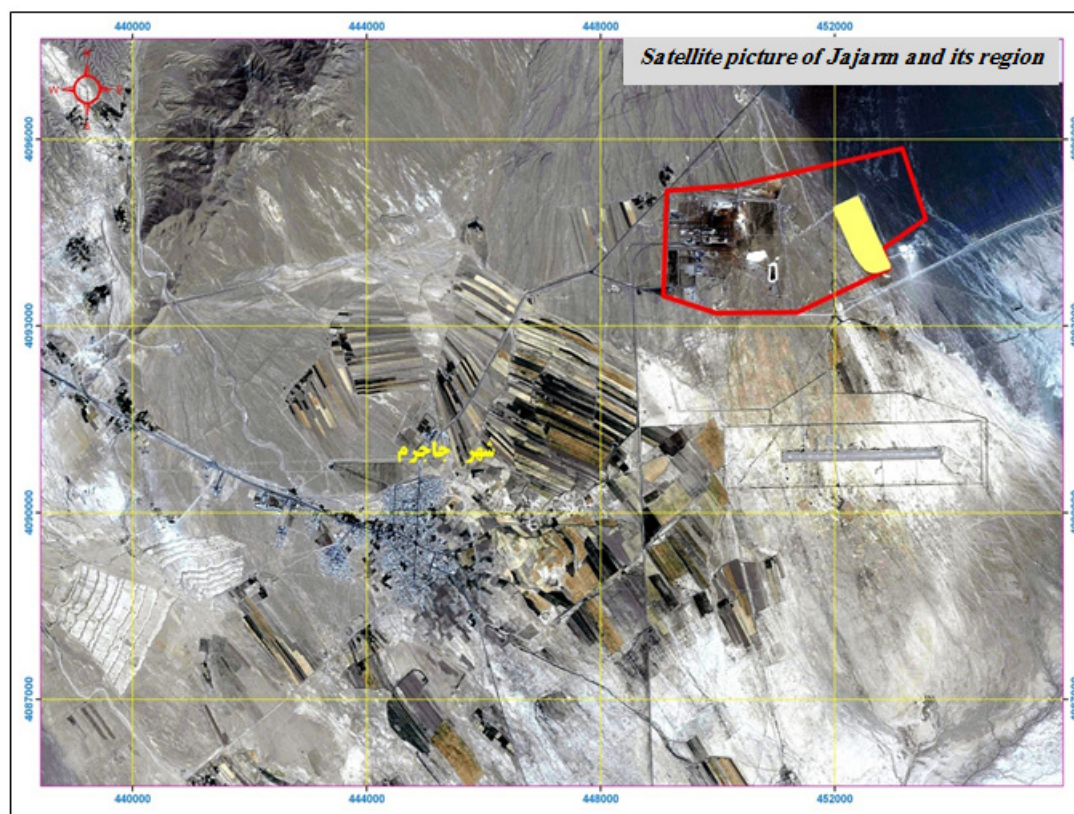
Table 2: The Method of removing heavy metals from wastewater

Number	Researcher	Data	Removal rate	Concentration (ppm)	pH	Metal	Removal method
1	Zhang et al (1993)[6]	Distribution coefficients	----- ----	100-200	5	Pb, Hg Cu	Cation exchange method
2	Yi-Ming-Gao et al (1995)[7]	Distribution coefficients	----- ----	200	5	Zn, Cd Cu, Pb	Ion Exchange
3	Jack Z (1996)[8]	pH, temperature, time, contact	85%	10-100	<6	Co Hg Pb, Zn, Se	Plant adsorption and ion exchange
4	Teruyuki U (1996)[9]	-----	90%	500	2	Fe	Under pressure Reactors
5	Rose (1998) [10]	pH, temperature, concentration	60 to 85%	500 to 3000	2- 8	Zn, Cu, Cd	Bio Sorbent
6	Young-Wook (1998)[11]	Time	98 to 100%	70 to 126	6	Zn, Cu, Cd, Fe, As, Al, Mn	No air reactor with a mixture of rice stalk lime
7	Feng (2000) [12]	Isotherm Adsorption	80-90%	942 113	1.65 5.12	Fe, Mn	Sequestration
8	Vivek (2001) [13]	Longmore Isotherm	Max 74 mg	700	3	Cu, Zn	Plant adsorption
9	Matthew (2002)[14]	Leaching results	80%	194 4.6	4.5	Fe, Mn	Chemical Sequestration
10	Chartrand (2003)[15]	Proton removal ability	80-90%	64 58	6-8	Fe, Cu	Electrochemical behavior
11	Tsukamoto (2004)[16]	Time effect	93%	100	3.5	Fe	Anaerobic treatment
12	Erdem (2004)[17]	Isotherm adsorption	----- ----	100-400	-----	Cu Zn, Mn	Attracted by the natural zeolite
13	Louis (2005) [18]	Geochemical model	99.95% 100% 85.7%	2500 10.5 15	6.5	Fe, Al, Ni	Passive operation (using alkalis)
14	Xinchao (2005)[19]	Time	98.6% 97.2%	172.5 88.6	3.5-4	Fe, Al	Selective Sequestration
15	Jacco (2006) [20]	Installing waste water meter	----- ----	660 19 337	4-6	Zn, Cu, Fe	Metal sulfide Sequestration



Table 3: Tailing characteristics of bauxite process of Jajarm factory

Solid components	48.59
Flow rate	102.48 cubic meters per hour
Mud type	Dry mud
Angle	° 3



(Fig. 1): Geographical location of bauxite Jajarm (The yellow color is tailing dam)

and has four rectangular shape bands. Red mud that is produced in the plant is carried by pipeline to the tailings dam which is located at 3 km east of factory. Figure 3 shows tailing characteristics of bauxite process of Jajarm factory [21].

Table 4 is a combination of Standards for Standard and Industrial Research Institute of Iran and presented standard by FAO and was suggested by Strategic Planning and Monitoring of vice-presidency [22].

### 1.3 Sampling and red mud analyzing

Twelve red mud samples were taken from different parts of the tailings dam of Jajarm bauxite factory and were homogenized. By analyzing granularity of homogenized sample d80 the obtained

sample is 48  $\mu\text{m}$  (Figure 2).

#### 1.3.1 The Physical properties of red mud

To measure some physical properties of red mud such as special density of solid percentage, and porosity, first a 250-ml graduated cylinder was weighed and filled with red mud. The cylinder and red mud in it were weighed again to obtain the pure red mud weight. Until red mud volume gets fixed on 150 mL (to be saturated), water is added. Some characteristics of red mud are shown in Table 5.

1 Special volume: total volume – volume of empty space

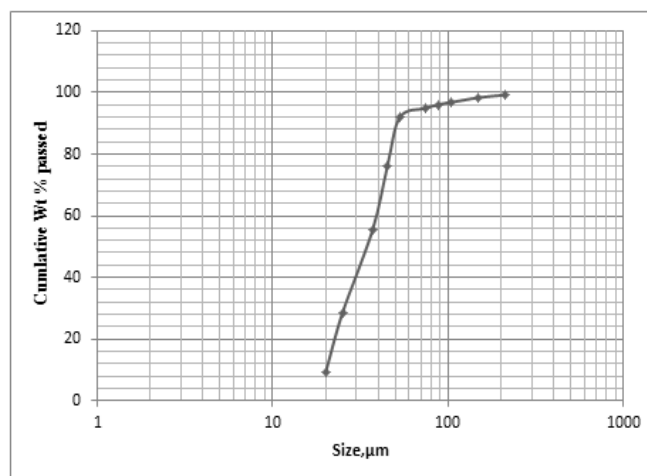
2 Bulk density: total weight / total volume

3 Specific density: total weight / special volume



Table 4: Standards of heavy metals for animal drinking

Reference	Row	Heavy metal	For animal drinking (milligrams per liter)
Institute of Standards and Industrial Research of Iran	1	Arsenic	0.2
	2	Aluminum	5
	3	Beryllium	-
	4	Bor	5
	5	Cadmium	0.05
	6	Chrome	1
	7	Copper	0.5
	8	Iron	-
	9	Lead	0.1
	10	Lithium	-
	11	Manganese	-
	12	Cobalt	1
	13	Lead	0.1
	14	Selenium	0.05
FAO, 1992	15	vanadium	0.1
	16	Mercury	0.01
	17	Zinc	34



(Fig. 2): screen Analysis of red mud

4 Porosity: volume of empty space / total volume red mud as eliminate and anatase.

### 1.3.2 XRD Analysis

Table 6 shows XRD analysis of red mud sample in tailing dam of Jajarm factory of bauxite; in which aluminum in tailing dam is located in compounds of hydro silicate sodium and calcium. Iron existed in tailing dam is as oxide hydro-oxide (hematite and goethite). Titanium is also existed in

### 1.3.3 XRF Analysis of red mud sample of tailing dam

Table 7 shows XRF analysis of red mud sample of tailing dam helping to determine the abundance of elements in the tailings dam. As it is shown in Table 7, iron, calcium, silicon, aluminum and titanium have the highest concentration of red mud.





Table 5: Physical properties of red mud

The total volume (ml)	150
Weight (gram)	122.45
Volume of empty space (ml)	85.51
Special volume (ml)	64.49
Bulk density (g/ml)	0.816
Special density (g/ml)	1.9
Solid percentage	0.43
Porosity	0.57

Table 6: XRD Analysis of red mud sample

Chemical formula	Mineral name (Phase)
$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3\text{-X}(\text{OH})_4\text{X}$	Katoite
$\text{FeTiO}_3$	Ilmenite
$\text{Fe}_2\text{O}_3$	Hematite
$\text{CaCO}_3$	Calcite
$\text{FeO}(\text{OH})$	Goethite

## 2. Materials and methods

### 2.1 Tank leaching test

In tank leaching test, water bath (to regulate and uniform dissolution temperature) is used with stirring - the electric motor, pH meter and beaker. In order to acidify the leaching solution to compensate for unrecoverable basic media used in pressurized bauxite processing procedure, the solution of sulfuric acid 33% was used. In each of the experiments carried out in a water bath, 20g soil samples were mixed at a pre-determined weight ratio of water to solid and were entered to the leaching tank for testing.

### 2.2 Test design

To identify the effective parameters for transferring heavy metals in tailing dam, at first with DX7 software (full factorial test design), 4 factors of temperature, pH, time and ratio of solid to liquid

phase have been studied in previous sources. By identifying the factors that influence the response of red mud leach, A model design (test design CCD) is obtained for more detailed study on each of the parameters. Parameters, high limits and low limits are presented in Table 8.

### 2.3 Materials and column leaching tests methods

In this work, eight columns (glass) with a diameter of seven centimeters and a height of 50 cm, were used. In upper part of the column, a layer of glass fiber with a diameter of three inches in between two sheets of Watman paper was used. At the end of the column, a layer of washed sand is placed between two sheets of paper. In order to control the flow, serum sets were used.

#### 2.3.1 Test Design

In column leaching tests three parameters of flow,

Table 7: XRF Analysis of red mud sample of tailing dam

Element (as oxide)	Concentration (%)
$\text{Al}_2\text{O}_3$	16.21
$\text{SiO}_2$	19.62
$\text{CaO}$	25.31
$\text{Fe}_2\text{O}_3$	28.02
$\text{TiO}_2$	6.87



Table 8: Effective parameters for transferring heavy metals in tailing dam and their high limits and low limits.

Parameters	Lower limits	Upper limits
pH	8	11
Temperature (°C)	20	50
The ratio of liquid to solid	1	10
Time (hours)	0.5	8



(Fig. 3): A view of Column leaching equipment

alkalinity, and time has been investigated which their high and low values are tabulated in Table 9 (DX7 and CCD was used). To adjust the acidity and alkalinity of a solution, sulfuric acid 95% and a 5% base was used. Before doing column leaching experiments and placing red mud into columns, materials were sieved by #270 and #325 mesh screens until the dimensions of red mud in them are 48 to 53 microns. By doing this, the effect of grain size on the leaching column reduces. Due to the low rainfall in the Jajarm and surrounding areas, the amount of flow was adjusted in low

level. In each column, 360 grams of red mud was poured. The height of red mud in each column is 15 cm. Based on test design, solutions with different pH were prepared in the one-liter container. Figure 3 shows the devices that were used in the column leaching tests.

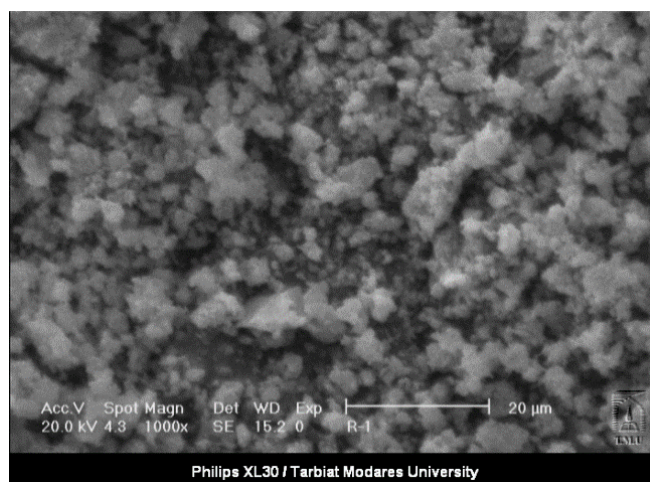
In each one of columns, 4cm red mud was poured and smashed until it was layered. In Table 9, there are lower and upper limits for each one of variable.

2.4 Adsorption condition and activation of red mud

In each of the experiments on the vanadium ad-

Table 9: Effective Factors in each column and lower and upper limits

Parameters	Lower limits	Upper limits
Entered flow	0.5	1
Alkalinity (gr / lit)	pH= 8	pH= 12
Time (Day)	8	24



(Fig. 4): SEM image of red mud activated in the process of adsorption

sorption by activated red mud, 1 ppm solution of vanadium by the volume of 10 ml was utilized (in the phase of effective parameters in vanadium transition that is obtained from the solid phase to the liquid phase).

In each of the experiments on the vanadium removal by activated red mud from the solution, first, at room temperature the red mud with granulation of #150-#200 mesh was processed by 10% hydrogen peroxide for 24 hours and then immediately was washed with water, dried at 100°C and cooled again at 500°C for 3 hours. Then, activation took place. This product was placed in a desiccator until using time.

#### 2.4.1 Test Design

In these analysis, three parameters of time, pH and the amount of absorbent is evaluated. The tests were designed by DX7 software (response surface methodology). Table 10 shows the upper and lower limits of these tests.

### 3. Discussion and conclusion

According to ICP results, the four elements of cobalt, nickel, arsenic and manganese were chosen in order to perform further analysis. Table 11 shows the analysis of 13 samples. These analyses are related to elements of nickel, manganese, arsenic, chromium, cobalt, uranium, titanium and iron. As it can be seen these metals did not transform to

liquid phase in laboratory condition.

#### 3.1 Investigating effective parameters in vanadium transfer to dissolved phase (Tank leaching)

According to the data obtained from test design conducted, best fitted model for inputs is:

##### 3.1.1 Effect of pH on vanadium leaching from red mud

Figure 5 shows pH effect on vanadium transfer to dissolved phase. As it can be seen in Figure 5, when pH increased from 8-12 the amount of vanadium transferred from liquid to solid increased from 0.56 ppm to 0.87 ppm.

##### 3.1.2 The effect of temperature on the vanadium dissolution

Figure 6 shows the effect of temperature (From 30°C to 50°C) on the vanadium dissolution.

When temperature increased the amount of vanadium dissolution increased as well. When temperature increased from 30°C to 50°C the dissolved vanadium increased from 0.54 ppm to 0.88 ppm.

##### 3.1.3 The Effect of time on the vanadium dissolution

Figure 7 depicted effect of time on the vanadium dissolution. Increasing duration of exposure of dissolution with red mud increases the transfer of vanadium from mud into liquid phase. When time increased from 3-7 hours, the vanadium dissolution increased from 0.49 ppm to more than 1 ppm.

Table 10: Parameters related to vanadium adsorption by activated red mud

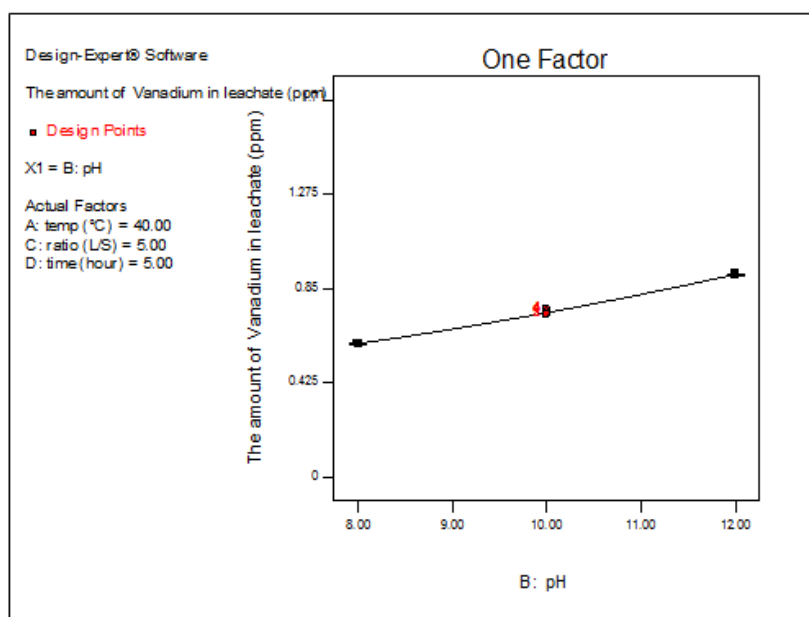
Parameters	Lower limits	Upper limits
Amount of absorbent (gram)	2	5
pH	12	9
Time (hours)	5	2



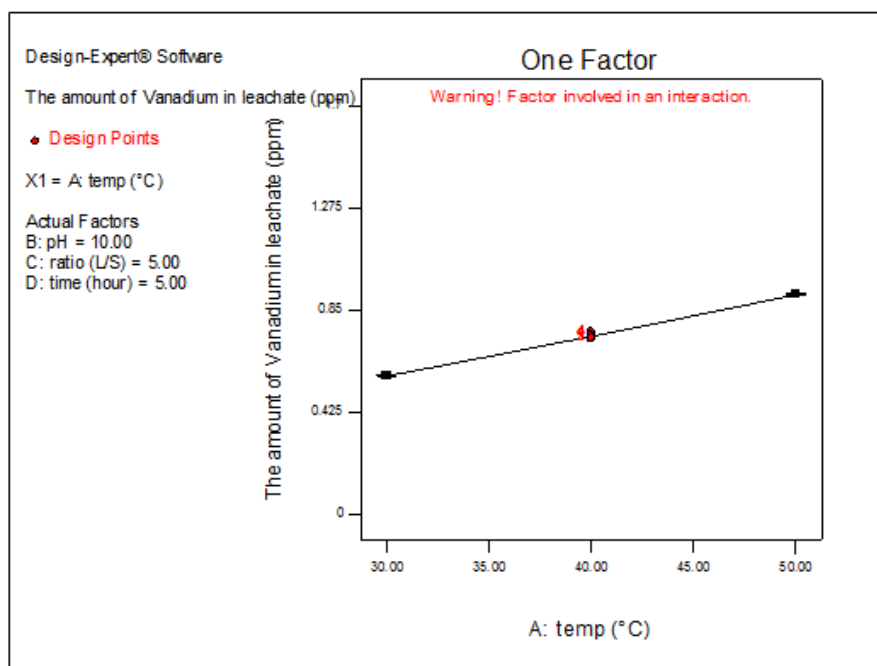


Table 11: Analysis of the concentration of elements changed to dissolved phase

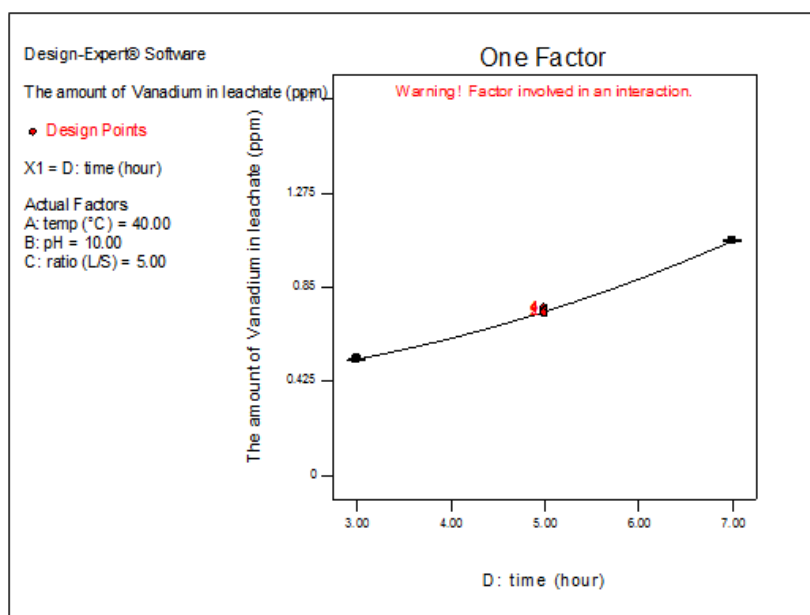
Number	Effective Factor				Heavy metal (ppm)						
	Temperature (°C)	pH	Time (hour)	Ratio (liquid/solid)	As	Co	Cr	Fe	Mn	Ti	Ni
1	50	11	3	10	Nd	Nd	0.006	Nd	Nd	Nd	Nd
2	20	8	3	10	Nd	Nd	0.065	Nd	Nd	Nd	Nd
3	50	8	8	4	Nd	Nd	0.074	0.042	Nd	Nd	Nd
4	35	9.5	10.5	7	Nd	Nd	Nd	Nd	Nd	Nd	Nd
5	35	12.5	5.5	7	Nd	Nd	0.045	Nd	Nd	Nd	Nd
6	20	12	3	7	Nd	Nd	0.027	Nd	Nd	Nd	Nd
7	20	12	8	4	Nd	Nd	0.017	Nd	Nd	Nd	Nd
8	20	8	8	4	Nd	Nd	Nd	Nd	0.005	Nd	Nd
9	20	11	0.5	1	Nd	Nd	0.023	0.001	Nd	Nd	Nd
10	20	8	8	1	Nd	Nd	0.005	0.003	Nd	Nd	Nd
11	50	9	8	5	Nd	Nd	0.007	0.007	0.001	Nd	Nd
12	20	5	10	5	Nd	Nd	0.008	Nd	0.001	Nd	Nd
13	35	4	5.5	7	Nd	Nd	0.012	Nd	0.002	Nd	Nd



(Fig. 5): Effect of pH on vanadium leaching from red mud



(Fig. 6): The Effect of temperature on the vanadium dissolution



(Fig. 7): The Effect of time (hour) on the vanadium dissolution

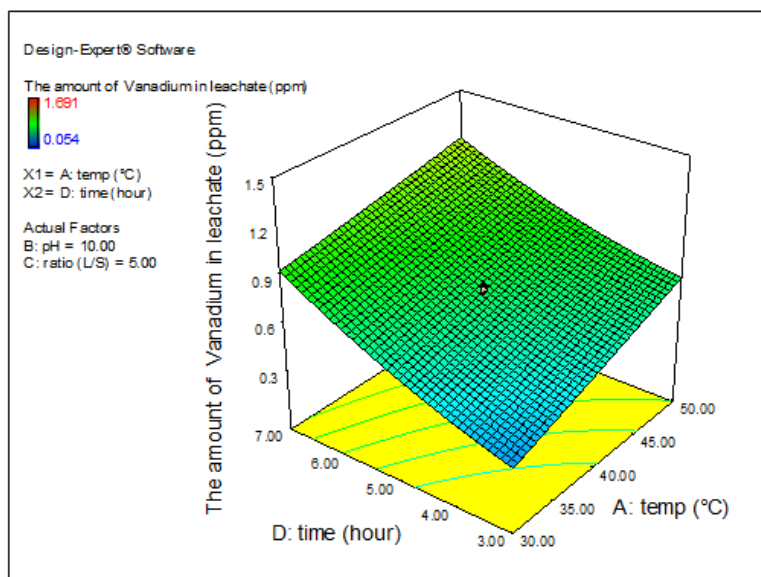
Evidently, two parameters of time and temperature have simultaneous effect on vanadium dissolution. This simultaneous effect is illustrated in Figure 8 by DX7 software. As it can be seen, by increasing time and temperature simultaneously, the amount of vanadium dissolution increased. As in 7 hours and 50°C the amount of vanadium transferred from red mud to dissolved phase increased to more than 1.17 ppm.

### 3.1.4 The effect of liquid to solid ratio on vana-

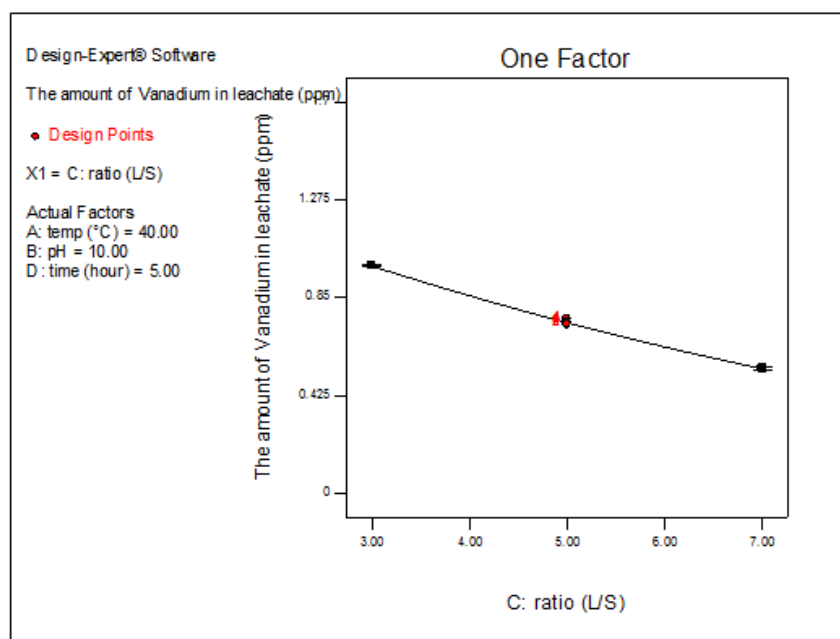
### dium dissolution

Figure 9 shows the transition amount of vanadium from solid to liquid in different ratio of liquid phase to a solid.

The reason of these changes in this test is that the rate of existing solid is assumed constant. In this case, the water consumption will be increased due to the increased amount of liquid to solid ratio. Therefore, the final amount of solution of the filter will be increased by increasing the ratio of liquid



(Fig. 8): Time (hour) and temperature (°C) simultaneous effect on vanadium dissolution



(Fig. 9): The Effect of liquid to solid ratio on vanadium dissolution

to solid and decreased vanadium (milligram) dissolution.

#### 4.1 Investigating effective parameters of the vanadium transition in phase solution (column leaching)

Based on results from test design (Appendix B) the best fitted model for inputs is;

##### 4.1.1 The effect of flow on the vanadium dissolution in column leaching

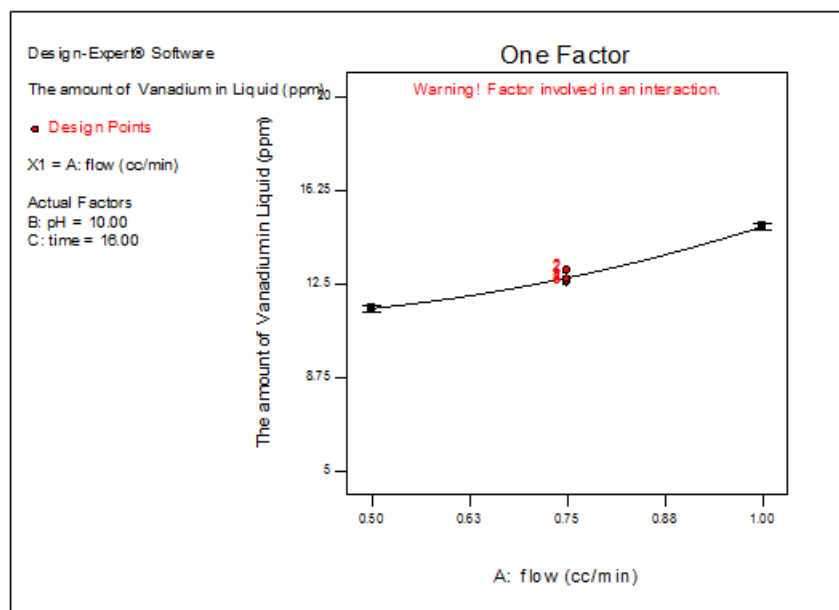
The effects of flow on the vanadium dissolution in column leaching was shown in Figure 10. As it is evidence, flow increasing from 0.5 min/cc to

1 min/cc caused vanadium transfer from the solid phase to liquid phase to surge from 11.5 ppm to 14.8 ppm (while based on Table 4, vanadium limit for livestock and poultry drinking is 1 ppm).

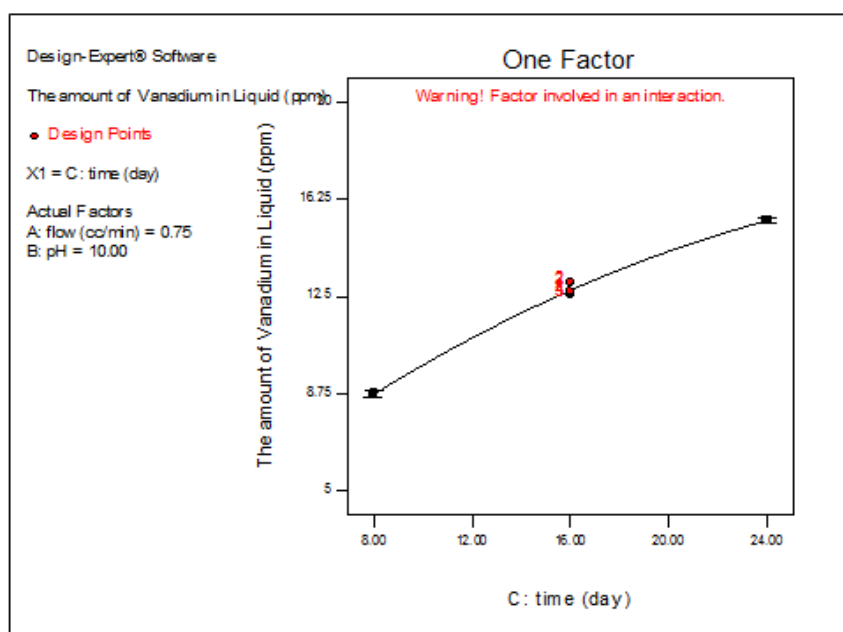
##### 4.1.2 The effect of time on the vanadium dissolution (column leaching)

Figure 11 shows the effect of time on the vanadium dissolution. Based on Figure 11, the amount of vanadium transferred to the aqueous phase is almost doubled with time increasing from 8 to 24 days.

As it can be seen, the slope of the curve follows a decreasing trend with increasing time. The amount



(Fig. 10): The Effect of Flow on the vanadium dissolution



(Fig. 11): The Effect of time on the vanadium dissolution in column leaching test

of vanadium in changeable phase was maximum 26 ppm and considering that vanadium dissolution was done in alkaline environment (according to the environmental conditions of the factory) vanadium phases change no more to dissolution, so we can say long time column leaching increase to maximum 26 ppm transfer vanadium to solution phase (the placement of vanadium in different phases were in previous study). However, this value is much larger than the allowed limit in water (based on Table 4, vanadium limit for livestock and poultry drinking is 1 ppm).

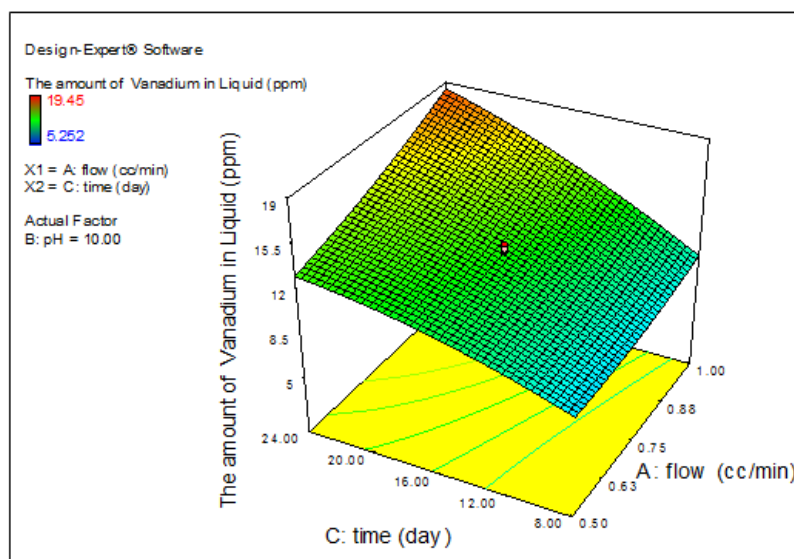
Figure 12 shows the Simultaneous effect of time

and flow on vanadium dissolution existed in red mud. With increasing flow rate (up to 1cc/min) and leaching time (up to 24 days) the amount of vanadium dissolved will increase significantly (up to 19 ppm).

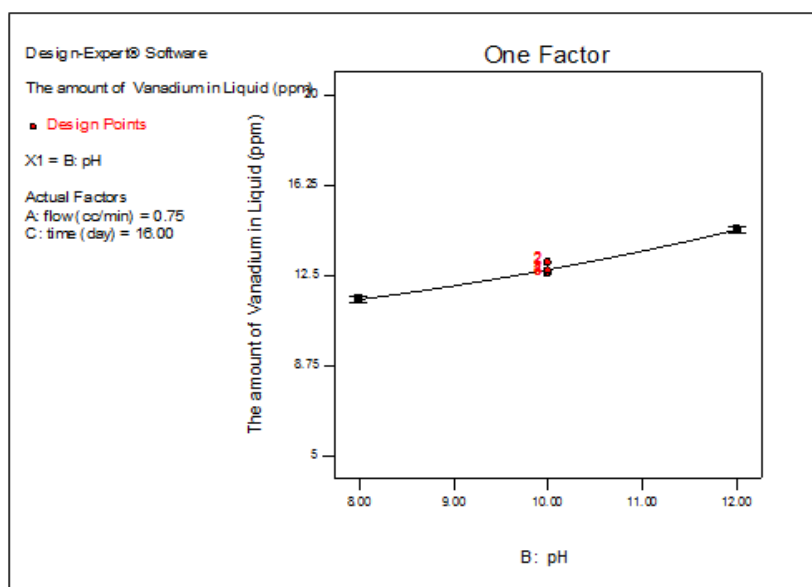
#### 4.1.3 The effect of pH on vanadium dissolution (column leaching)

Figure 13 shows the effect of pH on vanadium dissolution. As it can be seen with pH increasing vanadium dissolution rate increased.

#### 5.1 Using activated red mud for vanadium adsorption from solution



(Fig. 12): The Simultaneous effect of time and Flow on vanadium dissolution



(Fig. 13): The Effect of pH on vanadium dissolution in column leaching test

After doing designed tests by DX7, the best model coming from inputs is;

$$R = 52.446 + 1.429 \times \text{Dosage} + 1.291 \times \text{pH} + 1.844 \times \text{Time}$$

### 5.1.1 The effect of pH on vanadium adsorption from solution by activated red mud

Figure 14 shows the effect of pH on solution. As it is obvious in figure, with pH increasing from 9 to 12 the amount of vanadium adsorption increased from % 80 to % 85 in linear way.

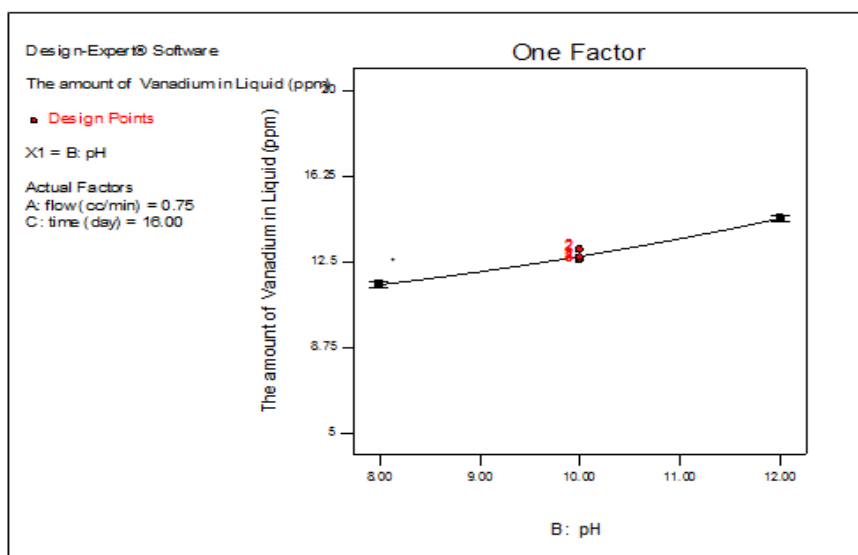
### 5.1.2 The Effect of activated red mud on vanadium adsorption from solution

Figure 15 shows the effect of activated red mud (grams) on vanadium removal from solution. As it can be seen increasing red mud in solution from 2 to 5 grams vanadium removal rate caused it increasing from %78 to almost % 85.

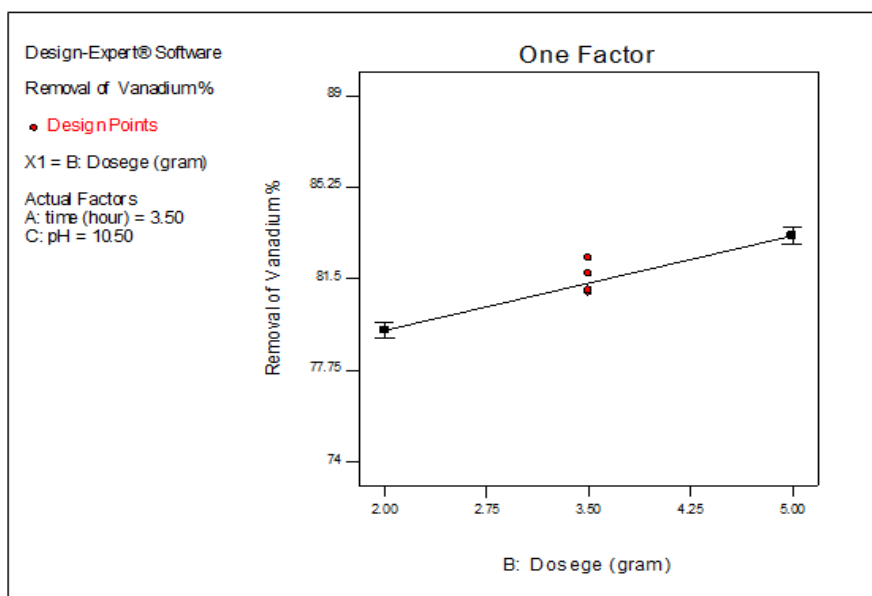
### 5.1.3 The Effect of time on vanadium adsorption by activated red mud

Figure 16 shows the effect of time on vanadium adsorption from solution. As in Figure 16, time increasing from 2 to 5 hours caused vanadium removal rate to increase from 79% to almost 85%.

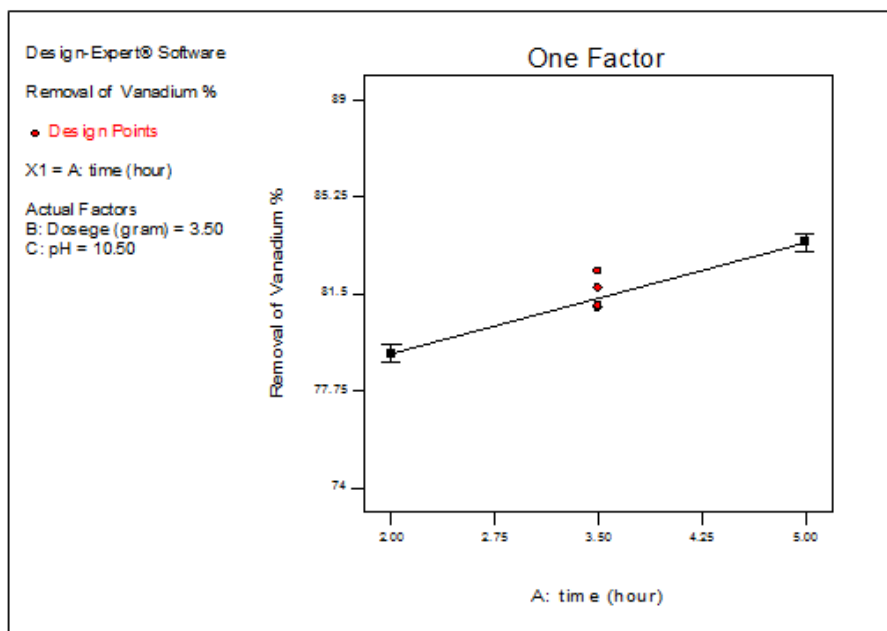




(Fig. 14): The Effect of pH on vanadium adsorption from solution (containing 1 ppm vanadium)



(Fig. 15): The Effect of activated red mud on vanadium adsorption from solution (containing 1 ppm vanadium)



(Fig. 16): The Effect of time on vanadium adsorption from solution (containing 1 ppm vanadium)

## 6. Conclusion

The analysis performed in this study determined that among all the dangerous heavy metals, only vanadium transforms to liquid phase at high densities. Maximum amount of vanadium transition from solid to solution occurs at pH=12, temperature; 60 °C for 8 hours and ratio of liquid to solid phase of 1. By doing column leaching tests it was determined that with increasing the input flow of 0.4 to 0.9 cc and at pH=7 dissolved vanadium percentage increases to %30. Moreover, increasing column leaching time from 3 to 30 days led to vanadium dissolution rate to be 2.5 times. If the pH

increases from 7 to 13, it will double the dissolution of vanadium. The most favorable conditions for the adsorption of vanadium by activated red mud was obtained at pH=12, density of 4.95 and time of 4.98. To decrease vanadium rate in aqueous solutions, it is suggested to reduce pulp pH before altering other parameters such as additives density and basic pulp density. For example, through using ferrous sulfate in addition to pH solution decrease (Due to the formation of sulfuric acid) due to the presence of Iron salts at high pH caused simultaneous deposition of metals such as vanadium.



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