

HEAVY METAL ASSESSMENT OF PHOSPHOGYPSUM WASTE STOCKPILE MATERIAL FROM JORDAN¹

M. Al-Hwaiti², V. Carney, J. F. Ranville, and P. E. Ross

Abstract: Phosphogypsum is a waste by-product of the phosphate fertilizer industry. The phosphate industry in Jordan has generated over 40 million tons of this waste material. Production continues at the rate of 3 million tons per year. The toxic heavy metal elements present in the by-product phosphogypsum and their effect on the human health and environment has prompted this study. The present study investigates potential toxic elements in phosphogypsum waste material from the Aqaba and Eshidiya fertilizer plants. Study parameters include concentrations and bioavailability of toxic elements, particle microstructure (SEM and XRD). Other variables considered include origin of deposit, age of deposit, particle size fraction and basic physico-chemical parameters. The results are used to determine the toxic element concentrations of phosphogypsum as well as to assess the impact of heavy metals that may pose a potential hazard to the human health and the environment from the two study sites.

Additional Key Words: heavy metals, distribution, phosphogypsum, bioavailability, Jordan

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Introduction

Phosphogypsum is a by-product of the chemical reaction called the wet process whereby sulphuric acid is reacted with phosphate rock to produce phosphoric acid, needed for fertilizer production. Approximately five tons of phosphogypsum is produced for every ton of phosphoric acid produced (FIPR, 1980; Anwar and Nadim, 1984 and Michael and Lloyd, 1985). Through the wet process, some impurities naturally present in the phosphate rock become concentrated in phosphogypsum, including fluoride compounds, heavy metals such as lead and cadmium, radioactive elements and residual acidity. The phosphate industry in Jordan annually produces 3 million tons of phosphogypsum stockpiled at Aqaba Complex for Fertilizer Industry and Indo-Jordan Fertilizer Company. The Aqaba Complex could accommodate over 30 million tons, while the Indo-Jordan factory at Eshidiya could accommodate 10 million tons (Fig. 1). The continued accumulation of phosphogypsum has created urgent pressures to find useful applications for this by-product.

The U. S. Environmental Protection Agency (EPA) has identified phosphogypsum as a potential hazardous waste because of its radium-226 content and the large volumes produced (Berta, 1990). The main impurities considered as pollutants in gypsum are heavy metals, particularly cadmium (Fergusson, 1990; Van Kauwenberg, 1997; Al-Hwaiti, 2000 and Brigden et al., 2002). May and Sweeney (1984) conducted research to determine if phosphogypsum is hazardous or toxic and, if so, to investigate means to mitigate the situation so that the phosphogypsum could be used in a variety of high volume applications.

The results indicated that trace elements were uniformly distributed in phosphogypsum stacks and showed no significant difference in the concentrations of trace element with depth. Thus, phosphogypsum was not a corrosive hazardous waste, if the pH was greater than 2. The presence of heavy metal contaminants may pose a potential hazard to human health (Roessler et al 1979; Taha and Seals, 1991; Cabrera et al., 1994; Davister, 1998 and Al-Masri and Al-Bich, 2002). Furthermore, Anwar and Nadim (1984) investigated the groundwater environmental aspects of phosphogypsum disposal as a function of the hydrologic conditions at the disposal site, and of the metal attenuation characteristics of various soil strata. He suggested that a gypsum stack will continue to drain until it stops settling due to self-weight consolidation and creep, and until moisture in the gypsum pore reaches field capacity. The time required for a closed stack to stop draining depends on the dimensions and age of the stack, the properties of the gypsum and the hydrogeological setting. A stack on porous foundation will drain much more rapidly than one constructed atop a low permeability clay stratum.

Al-Hwaiti et al (2005) studied the mobilization, redistribution and bioavailability of potentially toxic elements in Eshidiya phosphorites. They investigated the heavy metal distribution during the phosphate and phosphate fertilizer processing steps. All measured elements were enriched in phosphoric acid with the exception of As, which was enriched in phosphogypsum. Assessment of the availability of toxic elements to plants showed that Cd and Cr are not available for plant uptake, whereas Cu, Pb, V and Zn will be available upon direct application of phosphate to soil. Of the heavy metals present in the fertilizer, Cd is of greatest concern as a result of its toxicity, and ability to accumulate in soils, and its bioaccumulation in plants and animals (USPHS, 2000). In addition, The US Department of Health and Human

Services in its 9th Report on Carcinogens also lists cadmium and certain cadmium compounds as known human carcinogens (USPHS, 2000).

There is a clear association between the cadmium concentration in soil and the plants grown on that soil (WHO, 1992; Carter and Scheiner, 1992 and Elinder and Jarup, 1996). In 1989, EPA imposed a ban on phosphogypsum use under the National Emission Standard for Hazardous Air Pollutants (NESHAP) because of concern over radioactive elements and heavy metals in the phosphate used to manufacture phosphogypsum. The Florida Institute of Phosphate Research (FIPR) and other organizations believe they have demonstrated that phosphogypsum may safely and economically be used in building and road construction, agriculture and other applications. The increasing cost of land for stockpiles has promoted research on alternative beneficial uses of solid waste.

The objective of this work was to document the level of trace elements, with emphasis on heavy metals in phosphogypsum, in order to better understand the potential pollution problems that may pose hazards for public and environmental health associated with Jordan phosphogypsum.

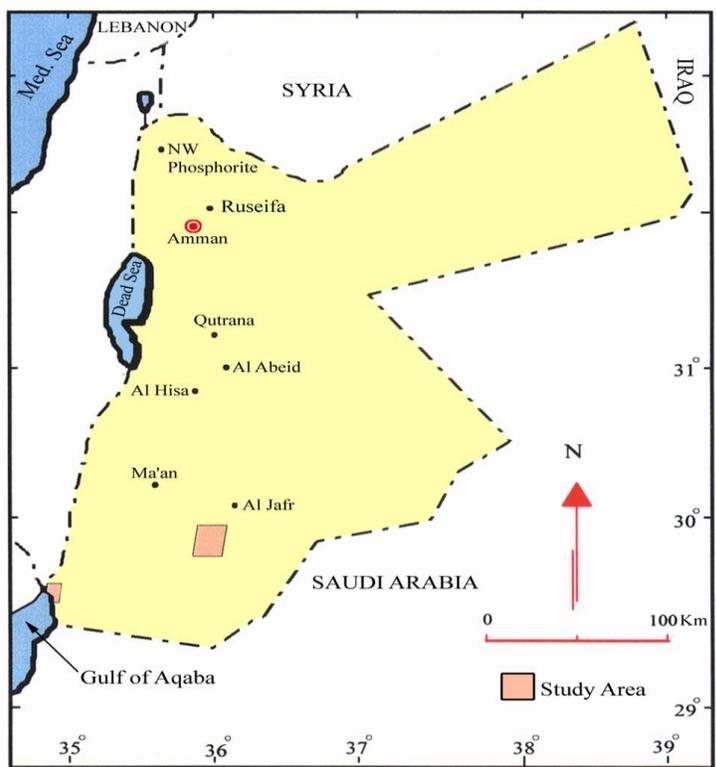


Figure 1. Location map of the study area. The Aqaba site is indicated by the shaded rectangle at the lead of Gulf of Aqaba. The Eshidiya is indicated by the shaded rectangle southeast of Ma'an.

Material and Methods

Sampling

Forty-eight samples were collected from the two facilities, Aqaba and Eshidiya. The samples were selected from 12 sites corresponding to piles of different ages depending on their

formation; 20 kg from each site were collected. All samples were dried, homogenized, sieved and ground into three particle size (sieve opening) ranges: Course > 0.212 mm; Medium – 0.212 to 0.053 mm and Fine < 0.053 mm. This was done to determine the trace elements distribution in different size fractions as well as whether the physical segregation might effect on trace elements distribution, as performed in experiments by May and Sweeney (1984).

Chemical Analysis

Partial Extraction. Fifty mg of each dried sample were put in a 15 ml centrifuge tube and 5 ml of nitric acid and hydrochloric (Aqua Regia) were added, then shaken and left for 24 hours. Afterward, the tube also was shaken and left an additional 24 hours, then centrifuged for 10 minutes. The supernatant solutions were prepared for chemical analysis by ICP-AES at the Chemistry and Geochemistry Department, Colorado School of Mines.

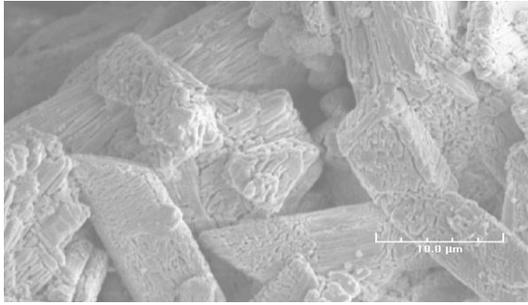
Total Extraction. Extractions were performed on 12 composite samples. This method has been developed by Paul Briggs at the U. S. Geological Survey (USGS). Twenty mg of composite sample were put in Teflon beakers, with 3 ml HCl, 2 ml HNO₃, 1 ml HClO₄ and 2 ml HF added to each beaker. Samples were dried on a hotplate overnight. 1 ml HClO₄ was then added and allowed to dry. The dried samples were removed from hotplate and cooled, 1 ml Aqua Regia was then added. A pre-set volume of 1 % HNO₃ was added to each beaker. The solutions were analyzed for U and trace elements by ICP-MS at the Savannah River Ecology Laboratory, Aiken, SC.

X-Ray diffraction Analysis (XRD). X-ray diffraction analysis was carried out at the Geology and Geological Engineering Department, Colorado School of Mines. XRD analysis was performed on composite samples of Aqaba and Eshidiya in order to determine the mineral composition of phosphogypsum. XRD of phosphogypsum powder mounts was in agreement with the earlier work of May and Sweeney (1984).

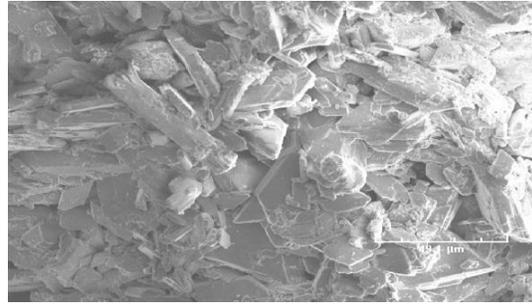
Scan Electron Microscope Analysis (SEM). SEM analysis was also carried out at the Geology and Geological Engineering Department, Colorado School of Mines. SEM was performed on composite samples of Aqaba and Eshidiya in order to identify the texture and structure of phosphogypsum.

Results and Discussion

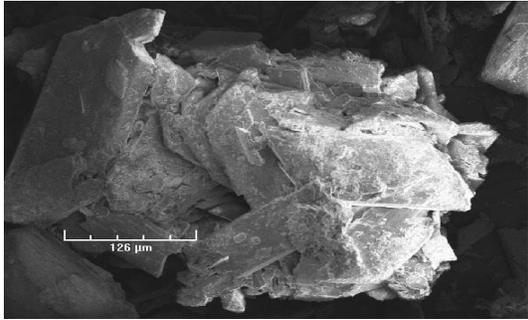
To understand the inter-elemental relationships between the analyzed elements, studying the phosphogypsum mineralogy was a priority. The XRD characterizations of the phosphogypsum detected gypsum and minor levels of quartz and mica. The limit of detection was about 5 % of mineral present. Fluorides and phosphates were present, as well as compounds of aluminum, magnesium, barium, iron and other elements. However, these compounds were present at less than 5 % and were not detected by the XRD. SEM examinations confirmed the presence of gypsum and minor quartz (Fig. 2). These results showed that there are different crystal shapes:



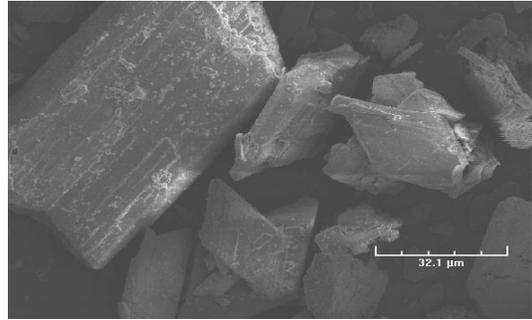
A



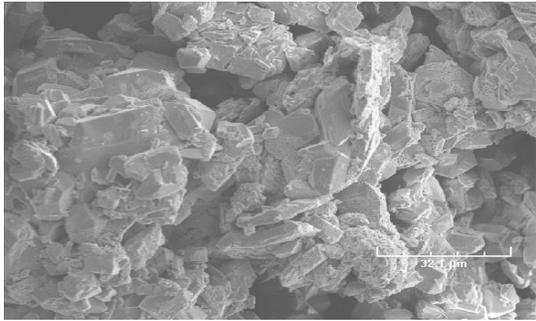
E



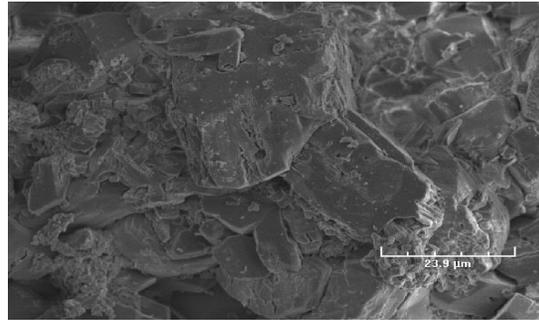
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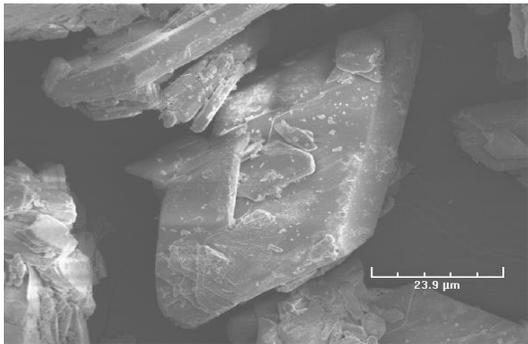
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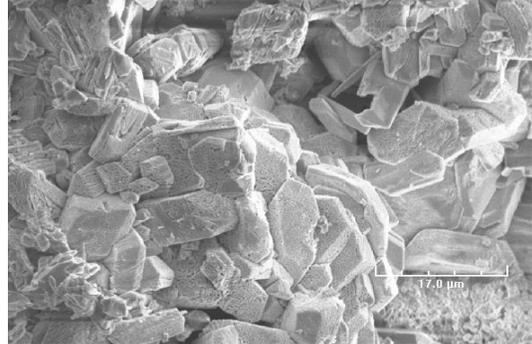
C



G



D



H

Figure 2. SEM showing crystal varies in size and shape, textures and aggregates of phosphogypsum, A, B, C and D from Aqaba and E, F, G and H from Eshidiya.

like needle-type crystals, small thin lozenges, rhombic, x-shaped swallowtail twins, flat type-like, cluster and the thick rhombic. These results were also confirmed by (Abdel-Al et al., 2004). It is clear that with increasing sulfate concentrations, there is formation of crystals at high sulfate and thick crystals at low super-saturation ratio (Abdel-Al et al., 2004).

Particle size distributions of trace elements are shown in Tables 1 and 2. The distribution was presented by coarse, medium and fine. All analyzed elements are enriched in the fine size fraction, with the exception of Na and Si (Table 1). These are enriched in the coarse size fraction, which might be attributed to the fact that these two elements are associated the quartz mineral phase as reported by XRD and SEM (Fig. 2). On the other hand, Al, Ba, Ca, Mg, S, P and V have variable distributions, whereas Fe, Na, Si are increased in the coarse size fraction in the Eshidiya phosphogypsum (Table 2). This is because these elements are likely associated with quartz.

Particle size distributions of heavy metals are shown in Tables 3 and 4. Arsenic, Mn, and V have variable distributions. Cr, Ni, and Se are enriched in the fine size fraction, while, Cu, Pb, and Zn, are enriched in the medium size fraction (Table 3). On the other hand, Cd, Co and Mo revealed no significant difference between the size fractions. Arsenic, Cr, Cu, Se and Zn show variable distributions (Table 4). V is enriched in the coarse size fraction, suggesting that it is associated with quartz mineral phase as reported by XRD and SEM. Cd, Co, Ni and Pb fairly uniform distributions

Correlations between the analyzed elements are shown in the figures 3 and 4. Calcium correlates positively with S and Ba in Eshidiya phosphogypsum with ($r = 0.94$ and 0.99 respectively) (Fig. 3). This indicates its association in gypsum mineral phase, as are revealed by XRD, SEM and fraction size distribution. In contrast, Ca shows strong negative correlation with Zn and Na with ($r = -0.87$ and -0.89 respectively). On the other hand, P has a positive correlation with As and Cr ($r = 0.79$ and 0.92) respectively, which might be attributed to these elements being associated with the phosphate mineral phase, as supported by XRD and SEM. The positive correlations between Si and Se ($r = 0.85$) and Si and Na ($r = 0.99$), suggest association in the quartz mineral phase as are reported by XRD, SEM and particle size distribution. Furthermore, Ca is correlated positively with S, Se and Zn in Aqaba phosphogypsum with ($r = 0.94$, 0.65 and 0.66 respectively) due likely to these elements being associated with the gypsum mineral phase as detected by XRD and SEM. Aluminum correlates positively with Cr, As, Ni, Mn and Cu ($r = 0.97$, 0.86 , 0.98 , 0.75 and 0.77 respectively) (Fig. 4). It seems likely that these correlations can be attributed to associations in aluminum compounds as are supported by XRD and SEM.

Table 1. Elemental (ppm) concentrations in aqua regia extracts of Aqaba phosphogypsum.

Aqaba	Material	Al	Ba	Ca	Fe	Mg	Na	P	S	Si	Sr	Ti
1 Y	Composite	3.39	0.27	272.40	1.20	0.22	12.64	34.19	230.46	10.22	3.18	0.01
	Coarse	3.56	0.27	263.06	1.16	0.22	10.92	32.25	220.85	9.50	3.28	0.01
	Medium	2.77	0.28	269.85	1.06	0.17	11.93	29.61	237.70	9.33	2.26	0.01
	Fine	3.61	0.42	324.46	1.22	0.23	7.76	33.12	258.15	7.40	4.12	0.01
5Y	Composite	4.58	0.35	244.31	0.85	0.38	14.95	42.74	199.86	15.86	3.57	0.01
	Coarse	5.14	0.21	235.18	0.87	0.35	12.66	42.96	180.84	14.93	3.88	0.01
	Medium	3.96	0.22	250.34	0.83	0.32	11.84	41.57	197.42	11.79	3.89	0.01
	Fine	4.02	0.35	253.08	0.86	0.33	8.79	43.02	203.85	9.72	4.16	0.01
10 Y	Composite	4.48	0.29	250.87	0.83	0.20	8.17	24.90	189.52	14.39	3.08	0.02
	Coarse	5.13	0.24	262.95	1.08	0.24	8.36	28.95	199.03	14.14	3.22	0.03
	Medium	4.46	0.23	259.49	0.82	0.19	5.96	25.32	191.96	14.00	3.39	0.01
	Fine	7.42	0.24	350.21	1.24	0.31	6.25	30.37	225.29	10.88	4.77	0.03
15 Y	Composite	4.97	0.18	247.60	0.83	0.42	14.48	49.47	199.86	11.88	1.65	0.05
	Coarse	5.04	0.23	295.95	0.96	0.53	11.59	58.74	225.11	12.33	1.92	0.05
	Medium	5.03	0.24	266.12	1.04	0.51	16.88	55.29	213.39	8.88	1.32	0.06
	Fine	7.09	0.29	313.41	1.21	0.73	6.15	78.03	223.78	3.66	5.39	0.07
20 Y	Composite	7.43	0.25	275.15	0.68	0.49	21.42	62.56	200.34	19.18	1.93	0.03
	Coarse	7.22	0.21	284.35	0.55	0.44	16.95	58.33	202.21	17.94	2.12	0.03
	Medium	6.10	0.22	266.25	0.70	0.42	14.08	47.76	204.31	12.40	1.42	0.03
	Fine	8.62	0.24	296.39	0.91	0.67	11.42	64.13	199.19	10.28	5.27	0.04
>20 Y	Composite	10.54	0.20	234.72	1.64	2.41	18.39	58.65	184.66	14.81	2.91	0.12
	Coarse	9.27	0.22	240.48	1.58	2.35	17.51	63.39	188.15	12.44	3.13	0.12
	Medium	9.29	0.20	249.17	1.55	2.40	18.86	56.60	197.55	12.27	3.03	0.12
	Fine	14.28	0.34	379.00	2.22	4.44	16.87	74.06	259.10	11.50	4.50	0.17

Table 2. Elemental (ppm) concentrations in aqua regia extracts of Eshidiya phosphogypsum.

Eshidiya	Material	Al	Ba	Ca	Fe	Mg	Na	P	S	Si	Sr	Ti
1Y	Composite	10.84	0.44	266.10	1.41	1.03	12.64	63.85	228.03	7.91	2.16	0.02
	Coarse	12.99	0.55	266.95	1.96	1.03	16.06	74.22	228.30	11.15	3.10	0.03
	Medium	10.29	0.51	273.01	1.29	0.73	13.46	58.90	239.84	8.09	2.74	0.02
	Fine	10.66	0.71	369.07	1.22	0.67	16.33	56.26	337.34	11.66	1.88	0.04
2Y	Composite	11.02	0.57	276.21	1.89	0.82	13.04	83.34	221.52	8.31	3.55	0.02
	Coarse	11.94	0.66	267.07	2.05	0.86	13.83	84.90	205.66	11.02	3.77	0.02
	Medium	12.04	0.65	256.71	2.04	0.87	14.37	84.66	206.91	7.29	4.02	0.02
	Fine	11.28	0.60	249.77	1.90	0.82	13.70	77.65	208.99	5.98	3.01	0.02
3Y	Composite	8.98	0.27	246.19	1.57	0.61	11.65	81.45	208.39	5.18	0.89	0.02
	Coarse	11.33	0.40	248.15	2.43	0.80	14.52	96.79	233.23	8.11	0.94	0.02
	Medium	10.67	0.38	283.17	2.16	0.73	13.34	92.16	238.10	5.51	0.84	0.02
	Fine	10.01	0.35	271.76	1.60	0.75	13.30	91.02	222.11	6.50	0.90	0.02
4Y	Composite	12.12	0.35	234.90	2.72	1.29	10.45	118.02	170.04	5.70	1.70	0.05
	Coarse	13.92	0.47	284.24	3.53	1.60	13.07	153.56	208.36	8.12	1.66	0.06
	Medium	13.07	0.49	272.78	2.94	1.42	12.40	124.47	213.87	5.85	2.15	0.05
	Fine	15.13	0.53	268.11	3.07	1.53	11.97	137.38	208.04	6.56	3.35	0.05
5Y	Composite	12.37	0.37	294.87	1.83	1.19	18.62	102.92	227.23	8.65	2.37	0.04
	Coarse	12.62	0.46	275.19	1.76	1.15	19.52	101.21	214.78	8.88	1.58	0.04
	Medium	13.53	0.49	302.89	2.00	1.33	17.31	101.47	211.62	8.27	2.90	0.04
	Fine	12.48	0.57	305.65	1.57	1.29	14.01	97.99	216.79	6.38	3.10	0.03
<5Y	Composite	13.83	0.42	279.96	3.14	1.58	14.04	153.16	210.41	9.42	3.02	0.05
	Coarse	15.80	0.50	296.96	4.19	2.05	15.93	183.96	208.96	12.82	3.11	0.06
	Medium	13.79	0.47	287.17	3.12	1.53	13.54	144.14	222.45	8.11	3.34	0.05
	Fine	14.47	0.46	288.03	3.48	1.72	14.50	160.42	213.94	10.12	3.16	0.05

Table 3. Heavy metal (ppm) concentrations in aqua regia extracts of Aqaba phosphogypsum.

Aqaba	Material	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Se	V	Zn
1 Y	Composite	0.12	0.01	0.02	0.04	0.06	0.02	0.01	0.22	0.01	0.18	0.02	0.09
	Coarse	0.10	0.01	0.02	0.04	0.08	0.03	0.01	0.22	0.01	0.15	0.05	0.04
	Medium	0.13	0.01	0.02	0.03	0.10	0.02	0.08	0.17	0.08	0.16	0.02	0.01
	Fine	0.11	0.01	0.02	0.04	0.07	0.03	0.02	0.23	0.02	0.18	0.02	0.10
5Y	Composite	0.22	0.01	0.02	0.04	0.03	0.03	0.01	BDL	BDL	0.14	0.02	0.11
	Coarse	0.05	0.01	0.01	0.04	0.08	0.03	0.01	BDL	BDL	0.10	0.02	0.12
	Medium	0.07	0.01	0.01	0.04	0.06	0.02	0.01	BDL	BDL	0.13	0.02	0.14
	Fine	0.23	0.01	0.02	0.04	0.03	0.02	0.01	BDL	BDL	0.14	0.02	0.10
10 Y	Composite	0.08	0.01	0.01	0.02	0.01	0.01	0.01	BDL	BDL	0.10	0.02	0.02
	Coarse	BDL	0.01	BDL	0.02	0.02	0.02	0.01	0.01	BDL	BDL	0.02	0.07
	Medium	0.05	0.01	BDL	0.02	0.03	0.01	0.01	BDL	BDL	BDL	0.02	0.03
	Fine	0.03	0.01	0.01	0.03	0.01	0.02	0.01	BDL	BDL	0.07	0.02	0.04
15 Y	Composite	0.03	0.01	BDL	0.03	0.01	0.01	0.01	0.01	BDL	BDL	0.03	0.05
	Coarse	BDL	0.01	BDL	0.04	0.10	0.01	0.01	0.01	BDL	BDL	0.03	0.31
	Medium	BDL	0.01	BDL	0.04	0.01	0.01	0.01	0.01	BDL	BDL	0.03	0.78
	Fine	BDL	0.01	BDL	0.06	0.02	0.02	0.01	0.02	BDL	BDL	0.05	0.10
20 Y	Composite	BDL	0.01	BDL	0.04	0.01	0.01	0.01	0.01	BDL	BDL	0.03	0.05
	Coarse	BDL	0.01	BDL	0.04	0.03	0.01	0.01	0.01	BDL	BDL	0.03	0.05
	Medium	BDL	0.01	BDL	0.04	0.04	0.01	0.01	0.01	BDL	BDL	0.02	0.08
	Fine	BDL	0.01	BDL	0.06	0.02	0.01	0.01	0.01	BDL	BDL	0.03	0.07
>20 Y	Composite	BDL	0.01	BDL	0.04	0.02	0.14	0.01	0.04	BDL	BDL	0.06	0.13
	Coarse	BDL	0.01	BDL	0.04	0.07	0.14	0.09	0.04	BDL	BDL	0.06	0.16
	Medium	BDL	0.01	BDL	0.04	0.05	0.14	0.03	0.04	BDL	BDL	0.05	0.15
	Fine	BDL	0.01	BDL	0.06	0.04	0.21	0.02	0.06	BDL	BDL	0.08	0.21

BDL = below detection limit

Table 4. Heavy metal (ppm) concentrations in aqua regia extracts of Eshidiya phosphogypsum.

Eshidiya	Material	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Se	V	Zn
1Y	Composite	0.13	0.02	0.03	0.05	0.04	0.20	0.01	BDL	BDL	0.21	0.04	0.12
	Coarse	0.14	0.02	0.03	0.07	0.08	0.25	0.01	BDL	BDL	0.23	0.05	0.17
	Medium	0.12	0.02	0.03	0.05	0.07	0.19	0.01	BDL	BDL	0.21	0.04	0.13
	Fine	0.13	0.02	0.03	0.05	0.03	0.20	0.01	BDL	BDL	0.22	0.04	0.09
2Y	Composite	0.14	0.02	0.03	0.07	0.01	0.24	0.00	BDL	BDL	0.22	0.05	0.16
	Coarse	0.11	0.02	0.03	0.07	0.02	0.27	0.01	BDL	BDL	0.19	0.06	0.16
	Medium	0.11	0.02	0.03	0.07	0.02	0.26	BDL	BDL	BDL	0.21	0.06	0.19
	Fine	0.13	0.02	0.03	0.07	0.01	0.24	0.01	BDL	BDL	0.22	0.05	0.16
3Y	Composite	0.13	0.01	0.03	0.05	BDL	0.12	0.01	BDL	BDL	0.22	0.05	0.02
	Coarse	0.11	0.01	0.03	0.07	0.02	0.15	0.01	BDL	BDL	0.22	0.06	0.04
	Medium	0.14	0.01	0.03	0.06	0.03	0.13	0.01	BDL	BDL	0.21	0.06	0.04
	Fine	0.12	0.01	0.03	0.06	0.01	0.13	0.01	BDL	BDL	0.23	0.05	0.03
4Y	Composite	0.13	0.02	0.03	0.10	0.01	0.28	0.01	BDL	BDL	0.20	0.10	0.08
	Coarse	0.13	0.02	0.02	0.12	0.04	0.35	0.01	BDL	BDL	0.21	0.13	0.12
	Medium	0.11	0.02	0.03	0.12	0.04	0.31	0.01	BDL	BDL	0.18	0.11	0.10
	Fine	0.13	0.02	0.03	0.12	0.01	0.31	0.01	BDL	BDL	0.21	0.13	0.00
5Y	Composite	0.11	0.02	0.02	0.11	0.01	0.17	0.01	BDL	BDL	0.19	0.01	0.06
	Coarse	0.11	0.02	0.02	0.11	0.03	0.15	0.01	BDL	BDL	0.17	0.01	0.07
	Medium	0.12	0.02	0.02	0.12	0.04	0.19	0.01	BDL	BDL	0.20	0.01	0.08
	Fine	0.13	0.02	0.02	0.10	0.01	0.18	0.01	BDL	BDL	0.21	0.09	0.07
<5Y	Composite	0.42	0.02	0.03	0.11	0.01	0.30	0.01	BDL	BDL	0.20	0.11	0.10
	Coarse	0.13	0.02	0.03	0.13	0.02	0.40	0.01	BDL	BDL	0.21	0.14	0.14
	Medium	0.11	0.02	0.03	0.11	0.07	0.29	0.01	BDL	BDL	0.20	0.11	0.24
	Fine	0.22	0.02	0.03	0.12	0.03	0.33	0.01	BDL	BDL	0.20	0.12	0.16

BDL = below detection limit

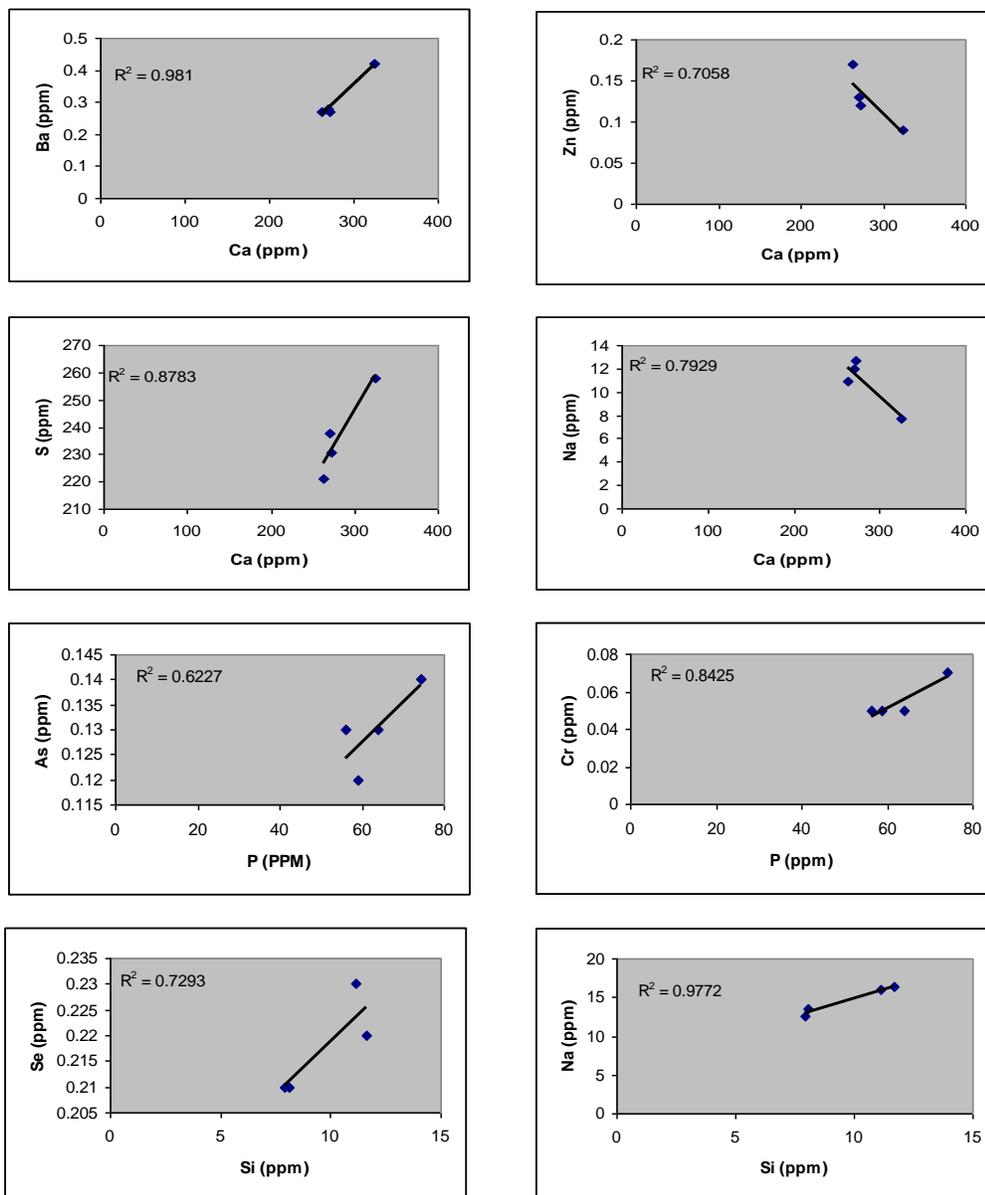


Figure 3. Correlation between elements in aqua regia extracts of Eshidiya phosphogypsum.

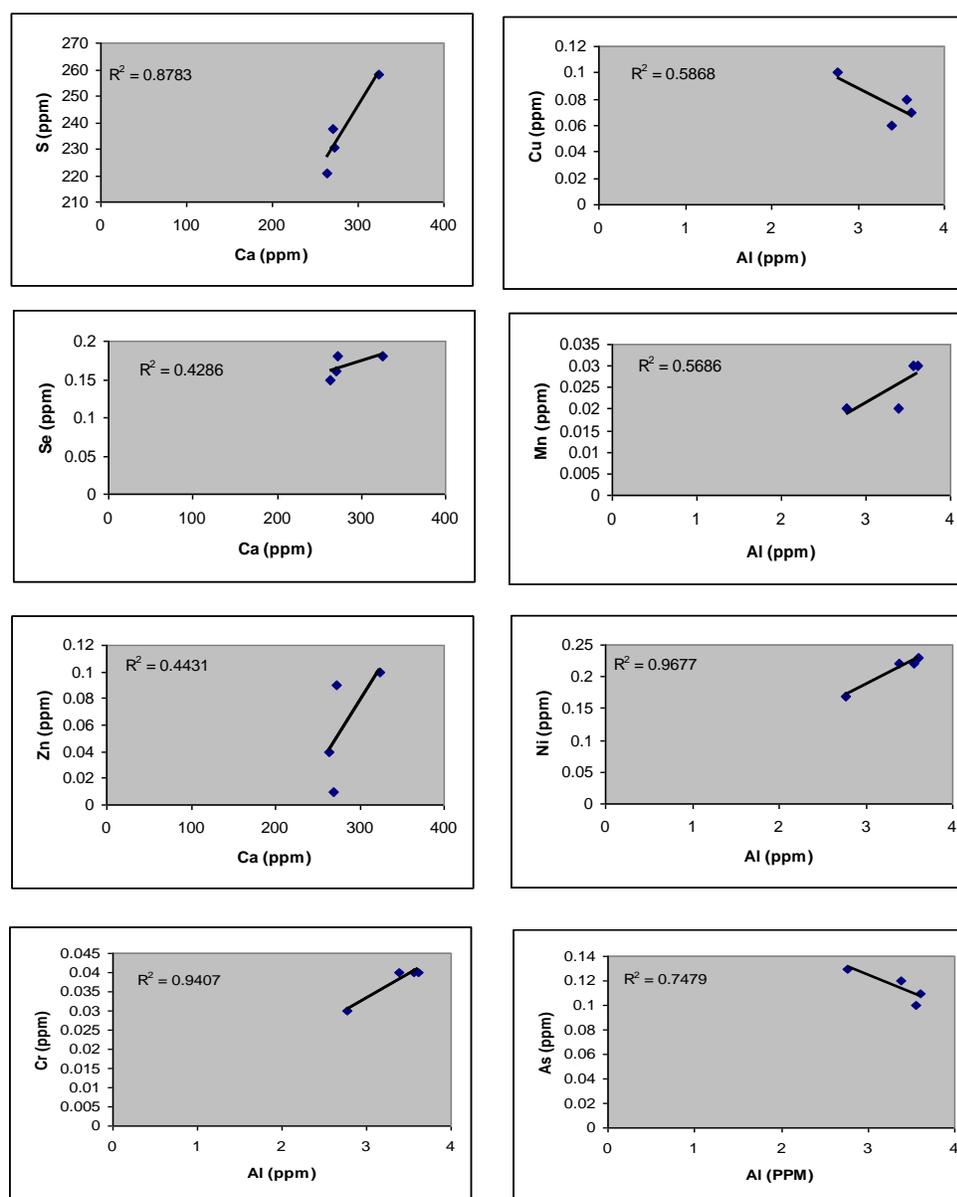


Figure 4. Correlation between elements in aqua regia extracts of Aqaba phosphogypsum.

In every case the previous results indicate that there were no significant differences in concentrations of the elements with age. These results indicated that trace elements were uniformly distributed in the phosphogypsum stacks. A uniform distribution of trace elements in a stack would occur if the same quantity of trace elements were added to the stacks as were removed through leaching. However, five stacks (5Y, 10Y, 15Y, 20 Y and >20 Y) are inactive at Aqaba phosphogypsum. Five stacks also are inactive at Eshidiya phosphogypsum; these are (2 Y, 3 Y, 4 Y, 5 Y and < 5 Y). These stacks are showed no significant difference in concentrations of trace elements with age. Thus, the results indicated that trace elements were not only uniformly distributed in the stack, but not leached from the stacks in any significant

amount. For comparison, the average concentrations of heavy metals in some World phosphogypsum and Jordan phosphogypsum are shown in Table 5.

Table 5. Elemental analysis of Aqaba and Eshidiya phosphogypsum compared to analysis from Florida (May and Sweeney, 1984) and Lebanon (Brigden, et al., 2002) phosphogypsum.

Element	Florida ppm	Lebanon ppm	Aqaba ppm	Eshidiya ppm
Al	1,360	-	8.81	7.81
As	42	1.5	0.11	0.18
Ba	7	<1	0.26	0.40
Cd	7	-	0.01	0.02
Co	2	<2	0.02	0.03
Cr	-	8	0.04	0.08
Cu	8	5	0.03	0.02
Fe	670	-	1.01	2.10
Mg	1,220	-	0.69	0.95
Mn	15	<1	0.04	0.22
Mo	16	-	0.01	0.01
Na	252	-	15.00	13.40
Ni	2	<2	0.07	B.D.L.
Pb	1	4	B.D.L.	B.D.L.
S	-	-	200.78	177.77
Se	-	-	0.14	0.21
Si	-	-	14.39	7.53
Sr	10	-	2.72	2.28
Ti	4,020	-	0.04	0.03
V	19	2	0.03	0.03
Zn	9	3	0.06	0.09

BDL = below detection limit

Obviously, all the analyzed heavy metals are depleted in Aqaba and Eshidiya phosphogypsum, and their average concentrations are significantly lower in comparison with those reported for Florida and Lebanon phosphogypsum.

A range of empirically derived extraction procedures has been developed over the years to simulate the availability of essential elements, and some toxic elements, to environment (Alloway, 1995). The techniques most widely used for phosphate rock and fertilizer employ a single extraction whose content for one element correlates with plant available content and can be used to predict plant uptake or likelihood of deficiency or toxic symptoms occurring in soil, plants or animals (Johnston and Proctor 1977; Bryan and Langston 1992; He and Singh 1994; Piotrowska and Kabata–Pendias 1997). In this study, the extraction reagent aqua regia was used, to bring together information on the behavior of heavy metals in phosphogypsum stacks. In addition to that, Motuzova and Ngo (1999) emphasized the influence of soil forming processes on the migration of elements from soil plant using correlation techniques. Therefore, in this study, some correlations were carried out in the sense of Motuzova and Ngo (1999).

The results of aqua regia leaching experiments on Aqaba and Eshidiya phosphogypsum are shown in Tables (6). To further assess the bioavailability and mobility of the analyzed elements, the calculated total element content (%) and correlation coefficients (r) were used as a measure

of the degree of bioavailability and mobility as shown in Table (7). For example, in Aqaba, a comparison of Cd values in the total extraction and the partial extraction at different age (1Y, 5Y, 10Y, 15Y, 20Y and > 20Y) shows that Cd contents are 0.41 and 0.01, 0.34 and 0.01, 0.81 and 0.01, 1.48 and 0.01, 1.19 and 0.01 and 1.43 and 0.01 ppm respectively. Accordingly, the extracted Cd amounts represent approximately 2.44%, 2.94%, 1.23%, 0.68%, 0.84% and 0.70% of original Cd present in phosphogypsum stacks Table (6). It is evident that Cd is very low in bioavailability and highly immobile especially from phosphogypsum stacks to soil. This conclusion is also expressed by the insignificant correlation (r) between total Cd content in phosphogypsum stacks and the amount of metal extracted by aqua regia as shown in Figures (5) and (6).

Aqaba and Eshidiya leaching results are listed in Table 6. This table illustrates the relationships between the elements contents in phosphogypsum and their corresponding values obtained by aqua regia extraction. The assessment results were then listed in Table (8) and (9). A careful examination of this table allows drawing the following conclusions: All the analyzed elements exhibit very low bioavailability with the exception of Se, which shows intermediate bioavailability in the Eshidiya phosphogypsum. Cd and Pb show immobility as compared to other analyzed elements, whereas Cr exhibits low mobility at Aqaba phosphogypsum and intermediate mobility at Eshidiya phosphogypsum. Copper and Zn shows intermediate to high mobility at both sites. Overall, the analyzed elements would not be expected to leach from phosphogypsum stacks to soils or ground water.

Table 6. Leaching experiments in aqua regia of Aqaba and Eshidiya Phosphogypsum

Phosphogypsum Site	Age	As ppm			Cd ppm			Cr ppm			Cu ppm		
		T As	Cx As	% TAs	T Cd	Cx Cd	%T Cd	T Cr	Cx Cr	%T Cr	T Cu	Cx Cu	%T Cug
Aqaba	1 Y	17.07	0.12	0.70	0.41	0.01	2.44	7.22	0.04	0.55	9.90	0.06	0.67
	5 Y	21.81	0.22	1.00	0.34	0.01	2.94	7.19	0.04	0.56	5.12	0.03	0.59
	10 Y	1.60	0.08	5.00	0.81	0.01	1.23	5.93	0.02	0.33	1.25	0.01	0.80
	15 Y	1.97	0.03	1.52	1.48	0.01	0.68	9.47	0.03	0.32	2.51	0.01	0.40
	20 Y	4.15	BDL	-	1.19	0.01	0.84	9.46	0.04	0.42	2.47	0.01	0.40
	> 20 Y	4.44	BDL	-	1.43	0.01	0.70	7.64	0.04	0.52	4.14	0.02	0.48
	Material	Pb ppm			Se ppm			U ppm			Zn ppm		
		T Pb	CxPb	% TPb	TSe	CxSe	% TSe	TU	Cx U	% TU	T Zn	Cx Zn	% TZn
	1 Y	2.04	0.01	0.49	0.87	0.18	20.69	1.01	-	-	24.02	0.09	0.37
	5 Y	2.26	BDL	-	1.58	0.14	8.86	2.32	-	-	23.90	0.02	0.08
	10 Y	1.31	BDL	-	0.47	0.01	2.13	2.42	-	-	5.93	0.02	0.34
	15 Y	1.76	BDL	-	0.25	BDL	-	3.97	-	-	16.51	0.03	0.18
	20 Y	1.04	BDL	-	0.73	BDL	-	8.86	-	-	20.22	0.03	0.15
	> 20 Y	1.09	BDL	-	0.00	BDL	-	5.90	-	-	37.38	0.06	0.16
Eshidiya	Material	As ppm			Cd ppm			Cr ppm			Cu ppm		
		T As	Cx As	% TAs	T Cd	Cx Cd	% TCd	T Cr	Cx Cr	% TCr	%T Cu	Cx Cu	% TCu
	1 Y	5.58	0.13	2.33	3.30	0.02	0.61	14.20	0.05	0.35	7.26	0.04	0.55
	2 Y	3.58	0.14	3.91	2.98	0.02	0.67	16.37	0.07	0.43	2.91	0.01	0.34
	3 Y	8.32	0.13	1.56	3.48	0.01	0.29	15.36	0.05	0.33	2.83	BDL	-
	4 Y	4.93	0.13	2.64	2.28	0.02	0.88	15.00	0.10	0.67	2.81	0.01	0.36
	5 Y	4.49	0.11	2.45	2.74	0.02	0.73	15.79	0.11	0.70	2.99	0.01	0.33
	> 5 Y	21.12	0.42	2.00	3.36	0.02	0.60	15.00	0.11	0.73	3.74	0.01	0.27
	Material	Pb ppm			Se ppm			U ppm			Zn ppm		
		T Pb	Cx Pb	% TPb	TSe	CxSe	% TSe	TU	Cx U	% TU	T Zn	Cx Zn	% TZn
	1 Y	1.76	BDL	-	0.63	0.21	33.33	2.69	-	-	32.06	0.12	0.37
	2 Y	0.90	BDL	-	0.28	0.22	78.57	2.46	-	-	32.60	0.16	0.49
	3 Y	1.07	BDL	-	0.30	0.22	73.33	5.11	-	-	14.98	0.02	0.13
	4 Y	0.73	BDL	-	0.39	0.20	51.28	7.57	-	-	24.60	0.08	0.33
5 Y	1.43	BDL	-	0.27	0.19	70.37	7.01	-	-	29.91	0.06	0.200	
> 5 Y	0.91	BDL	-	0.50	0.20	40.00	7.95	-	-	27.68	0.10	0.36	

BDL = below detection limit, Cx. : Extracted, T= Total, %TAs = (Cx As/ TAs) X 100%

Table 7. Total element content (%) and correlation coefficient (r) as a measure of the degree of bioavailability and mobility.

Total Element Content		Correlation Coefficients	
(%) ranges	Degree of Bioavailability	(r)	Degree of Mobility
0.01-24	Very low	0.00-0.24	Immobile
25-49	Low	0.25-0.49	Low
50-74	Intermediate	0.50-0.74	Intermediate
75-100	High	0.75-100	High

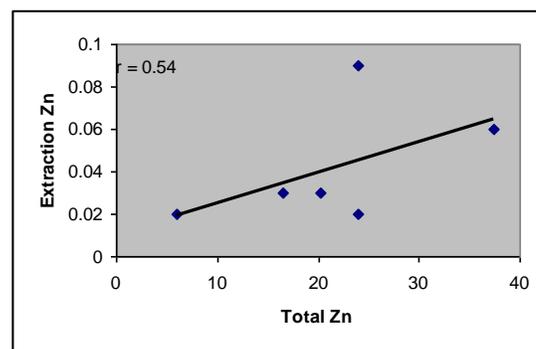
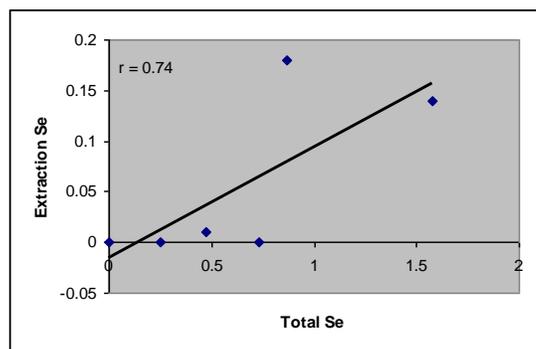
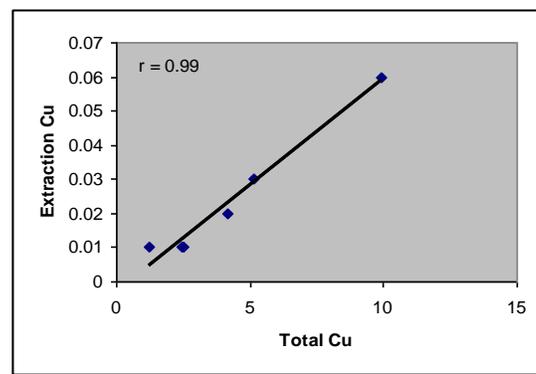
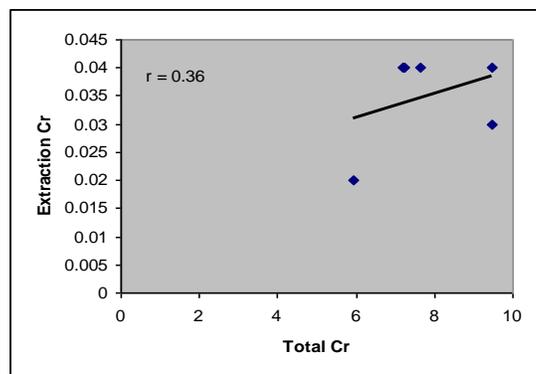
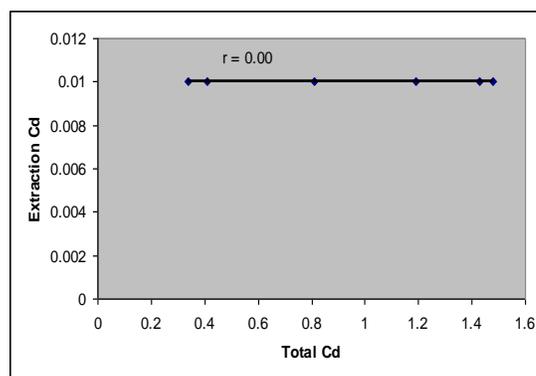
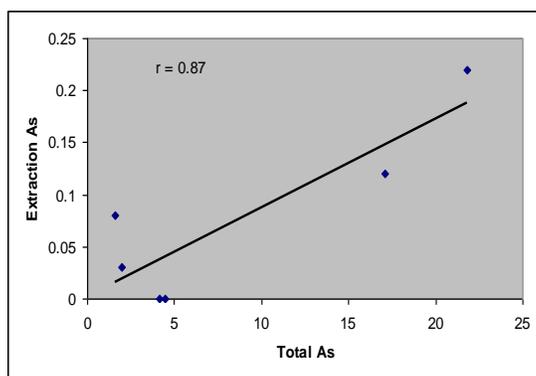


Figure 5. Relationship between the total heavy metals content (ppm) and their metal extracted (ppm) using aqua regia from Aqaba phosphogypsum.

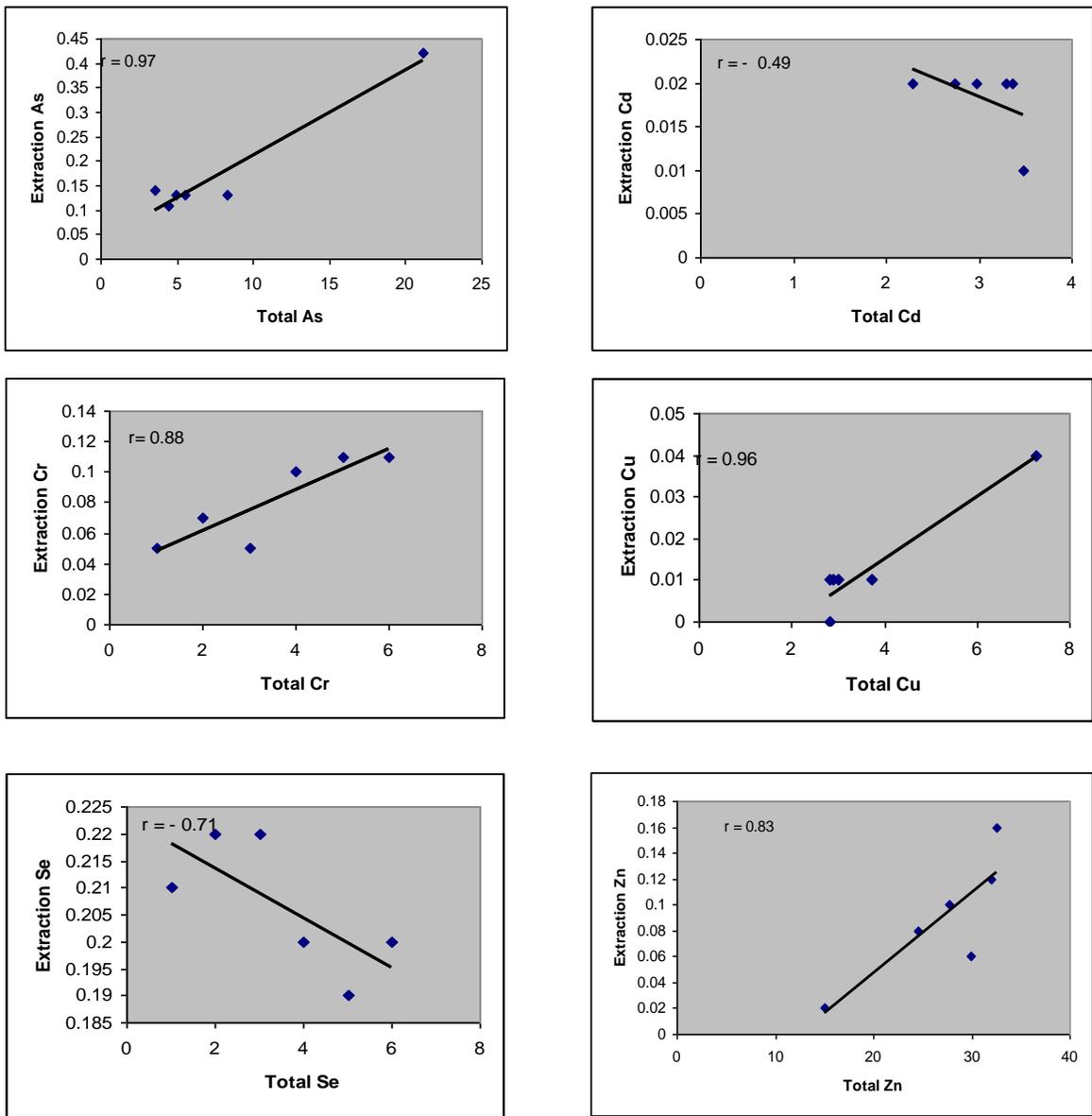


Figure 6. Relationship between the total heavy metals content (ppm) and their metal extracted (ppm) using aqua regia from Eshidiya phosphogypsum.

Table 8. Assessment element bioavailability and mobility of Aqaba phosphogypsum.

Element	Degree of bioavailability			Degree of Mobility			
	Age	(%)	Bioavailability	Overall Assessment	(r)	Mobility	Overall Assessment
As	1 Y	0.70	Very low	Very low	0.87	Intermediate	Intermediate
	5 Y	1.00	Very low				
	10 Y	5.00	Very low				
	15 Y	1.52	Very low				
	20 Y	0.00	Very low				
	> 20 Y	0.00	Very low				
Cd	1 Y	2.44	Very low	Very low	0.00	Immobile	Immobile
	5 Y	2.94	Very low				
	10 Y	1.23	Very low				
	15 Y	0.68	Very low				
	20 Y	0.84	Very low				
	> 20 Y	0.70	Very low				
Cr	1 Y	0.55	Very low	Very low	0.36	Low	Low
	5 Y	0.56	Very low				
	10 Y	0.33	Very low				
	15 Y	0.32	Very low				
	20 Y	0.42	Very low				
	> 20 Y	0.52	Very low				
Cu	1 Y	0.67	Very low	Very low	0.99	High	High
	5 Y	0.59	Very low				
	10 Y	0.80	Very low				
	15 Y	0.40	Very low				
	20 Y	0.40	Very low				
	> 20 Y	0.48	Very low				
Se	1 Y	20.69	Very low	Very low	0.74	Intermediate	Intermediate
	5 Y	8.86	Very low				
	10 Y	2.13	Very low				
	15 Y	0.00	Very low				
	20 Y	0.00	Very low				
	> 20 Y	0.00	Very low				
Zn	1 Y	0.37	Very low	Very low	0.54	Intermediate	Intermediate
	5 Y	0.08	Very low				
	10 Y	0.34	Very low				
	15 Y	0.18	Very low				
	20 Y	0.15	Very low				
	> 20 Y	0.16	Very low				

Table 9. Assessment element bioavailability and mobility of Eshidiya phosphogypsum.

Element	Degree of bioavailability			Degree of Mobility			
	Age	(%)	Bioavailability	Overall Assessment	(r)	Mobility	Overall Assessment
As	1Y	2.33	Very low	Very low	0.97	High	High
	2Y	3.91	Very low				
	3Y	1.56	Very low				
	4Y	2.64	Very low				
	5Y	2.45	Very low				
	>5Y	2.00	Very low				
Cd	1Y	0.61	Very low	Very low	-0.49	Low	Immobile
	2Y	0.67	Very low				
	3Y	0.29	Very low				
	4Y	0.88	Very low				
	5Y	0.73	Very low				
	>5Y	0.60	Very low				
Cr	1Y	0.35	Very low	Very low	0.88	High	High
	2Y	0.43	Very low				
	3Y	0.33	Very low				
	4Y	0.67	Very low				
	5Y	0.70	Very low				
	>5Y	0.73	Very low				
Cu	1Y	0.55	Very low	Very low	0.96	High	High
	2Y	0.34	Very low				
	3Y	0.00	Very low				
	4Y	0.36	Very low				
	5Y	0.33	Very low				
	>5Y	0.27	Very low				
Se	1Y	33.33	Low	Intermediate	0.71	Intermediate	Intermediate
	2Y	78.57	High				
	3Y	73.33	High				
	4Y	51.28	Intermediate				
	5Y	70.37	Intermediate				
	>5Y	40.00	Low				
Zn	1Y	0.37	Very low	Very low	0.83	High	High
	2Y	0.49	Very low				
	3Y	0.13	Very low				
	4Y	0.33	Very low				
	5Y	0.200	Very low				
	>5Y	0.36	Very low				

Conclusions

The XRD analysis and SEM analysis confirmed the presence of gypsum and minor quartz. The limit of detection was about 5 % of mineral present. Fluorides and phosphates were present, as well as compounds of aluminum, magnesium, barium, iron and other elements. Particle size distributions of analyzed elements revealed variable distribution of element concentration in different size fractions. Thus, the physical segregation results verified the results confirmed by XRD and SEM. Correlation between the analyzed elements was supported by XRD, SEM and particle size distributions.

Cadmium, Co, Ni and Pb exhibits relative uniformity in grain size distribution and at different ages. The phosphogypsum stacks showed no significant difference in concentrations of heavy elements with age. Thus, the results indicated that trace elements were not only uniformly distributed in the stack, but are not leached from the stacks in any significant amount.

The assessments of the bioavailability of heavy metals using aqua regia leaching experiments permit the following conclusion: All the analyzed elements exhibit very low bioavailability with the exception of Se, which shows intermediate bioavailability in the Eshidiya phosphogypsum. Cd and Pb show immobility as compared to other analyzed elements, whereas Cr exhibits low mobility in the Aqaba phosphogypsum and intermediate mobility in the Eshidiya phosphogypsum. Arsenic, Cu and Zn show intermediate to high mobility at both sites. Based on aqua regia, all analyzed elements exhibit different mobility in acidic environments ($\text{pH} < 2$). The mobility of all analyzed elements will decrease strongly in alkaline environments ($\text{pH} = 7$). Overall, the analyzed elements are not going to be leached from phosphogypsum stacks to soils or ground water. This indicates that there are no potential hazards to human health and environment from the both sites.

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