



ARSENIC POLLUTION FROM PHOSPHOGYPSUM PRODUCED AT MULTAN, PAKISTAN

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Phosphogypsum (PG) is a by-product of the phosphate fertilizer industry, which contains various toxic elements. The concentration of one of the toxic elements, arsenic, has been measured in 10 samples of PG waste collected from the stack of the Pak-Arab Fertilizer factory at Multan in Pakistan. The technique of instrumental neutron activation analysis (INAA) was employed for the characterization of this element. The quality assurance was controlled by analyzing the reference materials, IAEA-SL1, IAEA-SDM-2 and GSJ-JB-2 along with the PG samples. The concentration of arsenic was found to vary from 1.55 to 11.39 $\mu\text{g/g}$ with an average value of 6.26 $\mu\text{g/g}$. The level of arsenic in the PG samples was compared with the permissible value of this element in soil and water. The potential hazard of this element to human health and the environment has been discussed and method to control this pollution has been proposed in this paper.

Keywords: Arsenic; Phosphogypsum, Instrumental neutron activation analysis, Toxic elements, Industrial waste

1. Introduction

Phosphogypsum (PG), an acidic by-product of the phosphate fertilizer industry, is formed during the production of phosphoric acid from phosphate rock [1]. Phosphate rock, which is mainly composed of apatite $[\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})]$ is treated with concentrated sulfuric acid and water to produce phosphoric acid and hydrogen fluoride and the by-product gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Approximately 5 tonnes of PG are generated per tonne of phosphoric acid produced. The degree of calcium sulfate hydration depends on temperature and the operating acid concentration [2], and may increase during transport and storage of the PG. Different industrial processes involved in the production of phosphate fertilizers and the by-product PG are mentioned elsewhere [3]. The PG is mainly composed of gypsum with phosphorous content of less than 1%. The concentration of fluoride, certain naturally occurring radionuclides, and trace elements are usually relatively higher in PG and may pose a negative effect on the environment [1]. Major elemental composition of PG varies according to the type of wet phosphoric acid process used, while minor elemental concentrations vary greatly with the source of phosphate rock used for the production of

phosphate fertilizers [4]. A study conducted by Luther et al. [5] showed that PG originating from Idaho rock contains elevated levels of Ag, Cd, Se, Sr, As, some of the light rare earth elements, and Y relative to their concentrations in shale.

Arsenic occurs naturally in the environment as an element of the earth's crust, which is combined with other elements such as oxygen, chlorine, and sulfur to form inorganic arsenic compounds. Exposure to higher-than-average levels of arsenic occurs mainly in workplaces, near or in hazardous waste sites, and in areas with high levels of naturally occurring soil, rocks, and water. Exposure to high levels of arsenic can cause death, whereas its low level exposure for extended periods of time may cause discoloration of the skin and the appearance of small corns or warts. Phosphorite (phosphate rock) deposits are of mainly sedimentary origin, and are usually high in heavy metals content [6]. In addition to the several industrially important elements like Eu and La, phosphorite deposits also contain environment polluting elements like Cd, Hg, Pb, etc. [7]. Arsenic is also present in the phosphorite deposits. A study conducted by Sabiha-Javied et al. [8] on Hazara phosphorites deposits of Pakistan reveals that the concentration of arsenic varies from 9 to 24 $\mu\text{g/g}$ in

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these deposits. The presence of arsenic in phosphate rock leads to the transfer of this element to the fertilizer waste product PG.

Most of the PG waste is dumped in stacks near the fertilizer industry, which results in environmental contamination due to leaching and erosion of some of the constituents present in the waste that may further pollute the eco-systems, especially the ground water [9]. Another concern with storage includes surface runoff. Arsenate mobility is fairly low in acid soils whereas it increases in neutral to alkaline soils [10]. Also the pH of aged and leached phosphogypsum may approach neutrality [11]. Therefore, with the passage of time arsenic may be more mobile in the PG resulting in relatively higher contribution of arsenic to environmental pollution as compared to other elements present in PG waste in the study area.

In this work the concentration of arsenic has been determined in the PG generated by one of the phosphate fertilizer industry of Pakistan at Multan. Instrumental neutron activation analysis (INAA) technique has been applied taking into account the reference materials as comparators. Health and environment implications of PG due to arsenic have also been described.

2. Experimental Methods

2.1. Sample management

Ten samples of phosphogypsum (PG) were collected from a site adjacent to the Pak-Arab Fertilizer Factory at Multan. The samples were given the names; PG-1 to PG-10. The PG samples were collected in clean polyethylene bags and brought to the mineral processing laboratory at the Pakistan Institute of Engineering and Applied Sciences (PIEAS) located in Islamabad, Pakistan. Five specimens of 500 g were collected from each of PG site (four from each corner and one from the centre). The specimens were then mixed and one kg of samples was then obtained from the mixture called a PG representative sample. All samples were then ground to a powder, homogenized and passed through a sieve of 30 μm mesh size.

International Atomic Energy Agency (IAEA) reference materials (RMs) SL-1 (lake sediment) and SDM-2 (marine sediment) and Geological Survey of Japan (GSJ) JB-2 (basalt from Oshima,

Japan) were used as control materials. Multiple batches of about 50–100 mg of each sample and reference materials SL-1, SDM-2 and JB-2 were taken in pre-cleaned polyethylene irradiation capsules and further packed in polyethylene rabbits. Each batch contained three RMs and a PG sample in duplicate. The rabbits were thermally sealed and labeled prior to irradiation.

2.2. Elemental analysis

The sealed targets were irradiated in the periphery of the core of the Pakistan Atomic Research Reactor-2 (PARR-2), which is a 27 kW MNSR (Miniature Neutron Source Reactor) with a thermal neutron flux of $1 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. The targets were irradiated for one hour and counted for 900 s after cooling for one day. Before counting, the samples were transferred to pre-cleaned and pre-weighed polyethylene capsules.

The measurement system consisted of a CANBERRA model (AL-30) high purity Germanium detector (HPGe) attached to a PC-based multi-channel analyzer (MCA), (Inter-Technique model pro-286e) through a sensitive spectroscopy amplifier (ORTEC model 2010). The system resolution was 1.9 keV for 1332.5 keV ^{60}Co peak with a peak to Compton ratio of 40:1. Intergamma version 5.03 software was used for data acquisition. The data files, containing spectral information regarding peak energy, peak area, etc. were used in the indigenously developed computer program for activity and concentration calculations. This program makes corrections for background and incorporates any required decay factors.

The results were corrected for moisture content and reported on dry weight basis. Moisture content of the PG samples was measured by taking weighed amounts (about 4–5 g) of PG samples in clean, dry and pre-weighed vials. All samples were placed in an oven for 24 hours at 105 $^{\circ}\text{C}$. After removal from the oven the samples were kept in desiccators to cool. The samples were reweighed using an electronic balance. The ratios of dry to wet weight of samples were obtained using these measurements. The measurement uncertainties were estimated as given elsewhere [12].

3. Results and Discussion

The quality assurance of the elemental analysis was ensured by inter-comparison of the results of the reference materials IAEA SL-1, SDM-2 and GSJ JB-2 [13, 14]. The deviation of the measured results from the certified values is shown in Fig. 1. The overall precision for the measurement of the quantified element ranged within one standard deviation for all the three RMs. Values which differ from one another by ± 1 SD correspond to 99% confidence limit highlighting the reliability of our results. Arsenic was quantified using full energy peak at 559.1 keV that shows partial overlapping with 554.3 keV peak of ^{82}Br due to high count rate. This interference was overcome as discussed work by Mannan et al. [15].

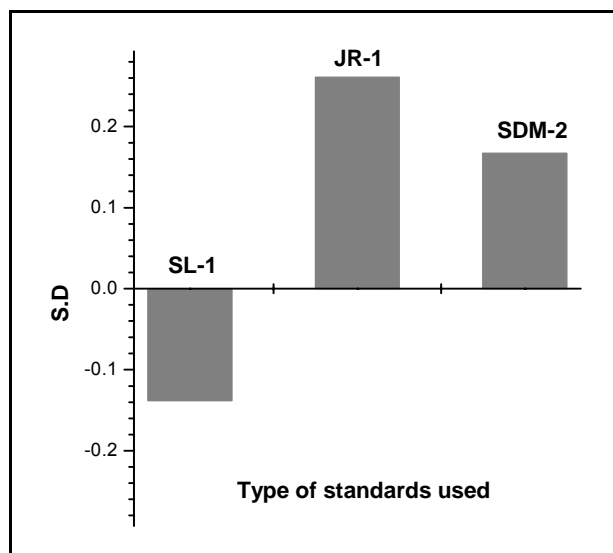


Figure 1. Control chart for the standards.

The concentration of arsenic measured in 10 phosphogypsum (PG) samples is given in Table 1 which varies between 1.55 to 11.39 $\mu\text{g/g}$ with an average value of 6.26 $\mu\text{g/g}$. The As concentration for sample PG-1 and PG-3 is the highest in the range of 11.21-11.39 $\mu\text{g/g}$, whereas for PG-4 and PG-6 comparatively lower concentration range of 6.05- 6.93 $\mu\text{g/g}$ is quantified. Sample number PG-2, PG-5, PG-8, PG-9, PG-10 have As values from 4.6-5.36 $\mu\text{g/g}$, however the lowest concentration was observed for sample PG-7. It is important to note here that the samples were collected on different days corresponding to different production batches. Since the type of phosphate rock employed in each batch may be different therefore the large variation in the As concentration in these

samples may probably be attributed to the type of phosphate rock being used for the production of phosphate fertilizer.

Table 1. The concentration ($\mu\text{g/g}$) of arsenic in phosphogypsum samples.

Sample I.D	Mean \pm S.D	% error
PG-1	11.39 \pm 0.89	7.84
PG-2	5.36 \pm 0.43	8.02
PG-3	11.21 \pm 0.45	4.03
PG-4	6.05 \pm 0.36	5.95
PG-5	5.2 \pm 0.51	9.82
PG-6	6.93 \pm 1.22	17.66
PG-7	1.55 \pm 0.42	27.17
PG-8	4.6 \pm 0.57	12.49
PG-9	5.14 \pm 0.46	8.93
PG-10	5.22 \pm 0.53	10.10
Min	1.55 \pm 0.42	
Max	11.39 \pm 0.89	
Average	6.26 \pm 0.75	
MDL*	0.50	

* Minimum detectable Limit

Table 2. Permissible level ($\mu\text{g/g}$) of arsenic in different environments.

Compartment	Permissible Level ($\mu\text{g/g}$)
Drinking Water	0.05
Irrigation Water	0.01
Agricultural soils	20
Agricultural soils for sensitive crops	5
Crops, fruits and Vegetables	2.6

The permissible concentration levels of arsenic in different ecosystems are given in Table 2. All the samples of PG under study show higher value of arsenic than the permissible level set for water [16], crops, vegetables, fruit and agricultural soil for "sensitive crops" (crops that are most susceptible to pesticide drift damage e.g. grapes, apples, strawberries, cane fruits, melons, tomatoes, broadleaf vegetables, some nursery crops and crops certified in an organic or naturally grown program) [17]. The comparison of arsenic concentration in PG samples with its permissible level in agricultural soils for sensitive crops shows that PG-2, PG-5, PG-8, PG-9 and PG-10 have As concentration comparable to the permissible level

of 5 µg/g in reference agricultural soil, however except for one sample (PG-7) all other samples of PG have higher concentration than the permissible level. Also this fertilizer factory when discharges its waste untreated to cultivated land causes death of livestock and increasing health risk to humans [18].

The permissible concentration level of arsenic in irrigation water is 0.01 µg/g; which is about 600 times lower than that of the average value of arsenic in the samples of PG under investigation. Taking into consideration that the PG samples contain very high amount of this element it is quite alarming situation for the general public and the health departments in particular that a small amount of arsenic if leached from the heaps of PG from the fertilizer factory is sufficient to contaminate the adjoining water body with arsenic. Moreover, arid atmosphere and stormy winds can also erode the PG waste to a large extent alongwith suspension of particulate matter in air. The city of Multan is located at 30°12' N and 71°27' E in the centre of Pakistan. It is extremely hot in the summer. The temperature in summer can be as high as 52 °C and in winter it can go down to 2 °C. Dusty and warm winds blow in the summer while July and August are the rainy months. These weather conditions of Multan are favorable for contamination of the air and water by PG waste through soil erosion and water leaching. It is also important to note that there are many canals that cut across Multan district that provide water from nearby rivers. The area around the city is a flat plain and is ideal for agriculture. Therefore, the water bodies and agricultural fields can come under the influence of PG waste contamination, which may lead to arsenic pollution.

The Pakistan Council of Research in Water Resources (PCRWR) and UNICEF have already declared that the groundwater of Multan region has relatively higher As concentration. Those studies revealed that deterioration in groundwater quality was due to disposal of untreated domestic and industrial waste in rivers and canals especially in high arsenic content reported cities [19].

Phosphogypsum waste may find many applications as it can be used as an additive to calcareous soil, as a special amendment agent for sugar cane, soybeans and peanut crops, as a raw material in plaster bricks and masonry walls,

binder for road construction, as an additive in composing beef cattle feedlot manure and as a feed additive for laying hens, etc. [20]. In addition the dumped PG waste is also used as a fertilizer because it contains small amounts of P₂O₅ [21]. Owing to the presence of large quantities of arsenic and toxic metals in PG waste, it is suggested that its applications as a feed supplement, should be restricted. The use of PG in agricultural fields for land leveling or land filling may contaminate the fields by the accumulation of the pollutant metals. Arsenic level will also be higher in the food crops produced in these fields. The soil of the Multan area is more alkaline in nature thus increasing the mobility of arsenic in such soil. Therefore the presence of arsenic in the agriculture soil may inhibit the growth of the cultivated crop [22] affecting both quality and yield of the crop. A study by Xiong et al. [23] reported the decrease by 10% of rice yield at a concentration of 25 mg/kg arsenic in soil whereas reduced yield of rice was reported by another study when irrigated with water having arsenic concentration in the range of 0.2–8 mg/L [24]. Human exposure to this element is mainly through soils, water, and diets. Most of the pesticides, herbicides, PG and other agricultural products contain compounds of arsenic and hence this element is leached into the soil and taken up by the vegetation.

The intake of the edible crops from such fields may increase the intake of this element and may pose serious concerns for risk to heart diseases, cancer of the skin, bladder, lung and other organs [25]. Arsenic is also reported to have the capability to pass through the human placenta and harm the unborn babies [26]. Typical findings are skin and nail changes, such as hyperkeratosis and hyperpigmentation etc. [27]. The estimated daily intake of arsenic per person through all types of diets should not increase its permissible safe levels of 120 µg [28]. However a lethal dose of arsenic (one-tenth of a gram) can also be achieved by a cumulative process over two months. Multiple sub-lethal doses received over a period of several weeks can accumulate in the body to achieve a lethal dose. Therefore, it is important to monitor arsenic concentration in agricultural fields, water bodies, food stuff, dust particles etc. so that our intake channels do not get contaminated by arsenic.

The waste management practices of the Pak-Arab fertilizer industry at Multan were also examined. These involve the dumping of the PG waste normally near the plant site. Therefore, it is also suggested that the present study should be expanded for routine monitoring of the environmental conditions of this area to reveal whether this practice is posing serious threat to the surrounding environment as PG waste when exposed to air may be contaminating both the soil and drinking water of this vicinity. Since the commercial uses of PG in agriculture and in manufacturing gypsum board are limited, therefore, a vast majority has to be disposed off. It is also recommended that Pak-Arab fertilizer should take care of the proper waste disposal management of the undesired PG.

The possible remedial measures should be undertaken where PG waste should be dumped in the suitable landfills instead of being dumped out in the open hence reducing its exposure to environment. Moreover, PG waste can be encapsulated before land filling which will further reduce the potential leakage of pollutants to ground water. The better and effective way to reduce pollution from PG is to use it as a road base which is cheaper and effective than compared to any traditional road base materials. Routine monitoring of As is also recommended in all PG waste dump sites.

4. Conclusions

To determine the concentration of arsenic in phosphogypsum (PG) of Pak-Arab Fertilizer Factory at Multan, 10 samples of PG have been assayed using the technique of instrumental neutron activation analysis (INAA). Arsenic was quantified in the range of 1.55 to 11.39 $\mu\text{g/g}$. The amount of arsenic in seven samples (PG-2, PG-5, PG-8, PG-9, PG-10) was determined to be in the range and of its permissible limits in agricultural soils for sensitive crops. However, PG-7 showed lower values, whereas the rest of the samples showed higher limits. The population living adjacent to the fertilizer factory area is inadvertently exposed to the pollution of PG waste. Arsenic leaching from the PG stacks is a potential contaminant for water bodies and agricultural fields from where it is transferred to the food chain and may lead to an increase in the concentration of As; beyond the permissible levels. Therefore, proper management for the disposal of PG is required. As

arsenic is a potential health hazards, it is imperative to remove it from the PG waste prior to its disposal.

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