

ANALYSING THE CHARACTERISTICS AND APPLICATION POTENTIALS OF JAROSITE WASTE IN KOSOVO

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ABSTRACT

Jarosite waste released from the zinc production process during the hydrometallurgical leaching of concentrates in Trepça lead-zinc smelter, Kosovo has serious environmental problems due to the presence of toxic metals such as Pb, Cd, Zn, As etc. Its disposal in open tailing dumps has become a major environmental concern with contamination effects of water, soil and vegetation. The current paper considers the jarosite waste in Mitrovica Industrial Park, Kosovo in order to evaluate the characteristics of jarosite waste, identify the potential environmental impacts and understand its potential for recycling or utilization as a challenge for the development of a positive “green” image environmental protection and sustainable hazard waste management in future. XRD, SEM and TG/DTA were used to analyze the characterization features of jarosite. The results give an initial understanding of the jarosite strengths and application potentials as recycled material. The potential application provides useful contribution towards proper environmental, social and economic management development.

Key words: jarosite waste, characteristics, application

1. Introduction

Worldwide, the jarosite process is the most widely used technique of iron removal from the acidic process in the zinc industry, where it is often produced as a by-product. The use of jarosite in the zinc industry was followed with the production of iron precipitates; minimum losses of Zn, Cd and Cu in jarosite precipitates. During the zinc production process huge amounts of jarosite is released as waste, where the jarosite are extremely common. Therefore, the jarosite is common in diverse environments such as: nature (oxidising zones of sulphides deposits, acid sulphate soil or clays) and metallurgical waste (Baciano and Peterson, 2007). Even though the function of jarosite as potential source of acid in a mine is not completely understood, the traditional view that acid can be generated in mine waste due to the oxidation of sulphide minerals and dissolution of sulphate salts and sulphate minerals such as jarosite, has been brought to the attention by several researchers (Baciano and Peterson, 2007; Frost *et al.*, 2005; Buckby *et al.*, 2003). Jarosite waste, originating from zinc production industry, is considered hazardous due to the presence and the mobility of toxic metals that it contains. Its worldwide disposal in many tailing dumps has become a major environmental

concern. In order to avoid the environmental problems caused by the disposal and uncontrolled leaching of hazardous waste, the researchers are making great efforts in developing different cleaner processes (Yang *et al.*, 2009; Yasuda, 1991; Jha *et al.*, 2001; Zhao-hui *et al.*, 2010; Boura *et al.*, 2003; Lee and Pandey, 2012; Farmarzi *et al.*, 2004; Asta *et al.*, 2009; Pelino, 2000). However, very few papers have been published on recycling and the utilization of jarosite. The increase of economic and financial factors dictate that the industry should look forward for development of better opportunities with regard to the recycling or reusing of the industrial hazard waste.

In Kosovo industries about 30.000 ton/year zinc, 67.000 ton/year sulphuric acid, 115 ton/year cadmium and 1.500 ton/year zinc alloy is being produced. As a consequence huge quantity of jarosite is being released that beside the economic benefits led to severe environmental damages and very often with serious health hazard for the workers and resident population living close to the industrial area and Trepça Mining Complex. Today, Trepça Mining Complex is identified as one of the biggest environmental hot spots in the region with toxic/acidic effluents, uncontained waste rock, contaminated building facilities, dust emissions and unsecured working environments, poorly contained and unstable tailing waste. Mining and mineral processing in Kosovo has been characterized by large open tailing dumps with a large amount of waste disposed. At present industrial waste tailing dumps and opencast mines cover more than 10 000 hectares. It is estimated that over 40 000 000 million tons of waste are accumulated in tailings within the region (UNEP, 2010; Rydergren and Montelius 2004; Frese *et al.*, 2004; Brininstool, 2010). Therefore, the mining waste management is a major challenge for Kosovo due to the poor management and disposal, little interest in reducing the quantity and hazardousness waste or recycling. The unsolved environmental problems are considered as a major obstacle for the region that prevents potential economic benefit. Further development of chemical industry sector is hampered by lack of investment and lack of environmental management. There have been identified poor monitoring systems that measure the environmental impact of industrial waste. For the environmental assessment to be effective, data collection and analysis are very important in order to ensure the effectiveness and accuracy of the waste management and also to identify the best utilization possibilities of the present types of waste.

This study demonstrates the jarosite waste characterization and the mobility of heavy metals present in jarosite tailing waste in Mitrovica Industrial Park, Kosovo. In particular, the study intends, on one hand to solve the problem of environmental pollution by transferring the negative features of jarosite waste into the positive contribution through neutralizing the harmful characteristics and on the other hand, the work performed to contribute obtaining valuable materials from jarosite waste with an economic benefit. In order to achieve the underlying objective the toxicity leaching characteristics was applied to estimate the amounts of potential toxic elements and potential ecological risk of the tailing waste and to provide theoretical basis for possible recycling of this kind of waste. The jarosite waste in Kosovo was characterized using XRD, SEM and TG/DTA techniques. A comprehensive utilization of jarosite waste from zinc industries to compensate resources shortage and environmental protection will have enormous economic and social benefits.

2. Materials and methods

2.1. Sample Collection and Preparation

The investigation site contains metallurgical waste identified as jarosite waste deposited in an open tailing dump in Mitrovica Industrial Park (MIP). MIP is situated very close to a residential area of southern part of the Mitrovica town, 20 m next from the banks of Sitnica River. This park comprises of a zinc refinery, battery factory, fertilizer factory and around 35 h covered with industrial waste. At present tailings in Mitrovica Industrial Park contains over 1.5 million tons of waste, out of which 500 thousand tons of this waste originates from jarosite process of the Trepça zinc industry. This type of waste is serious threat for the environment and

health due to the high content of toxic metals in waste. The tailing material can be spread to the environment by the wind, erosion or through various chemical reactions. Within the sampling framework the jarosite samples were collected from open tailing damp. After sampling, jarosite waste was air-dried at room temperature, sieved through 2 mm size sieve, mixed and homogenized using coning and quartering method and stored in polyethylene containers until analyzed.

2.2. Chemical analysis

The waste composition was determined by means of inductively coupled plasma - optical emission spectrometry (ICP-OES) using the assisted microwave digestion method (HCl/HF/HNO₃/H₃BO₃). In order to evaluate the stability and accuracy of the procedures in the analysed jarosite samples, the reference material was used (S JR-3 and S Jsy-1) with the same procedure. All reagents used in this work were analytical or HPLC grade and used without any further purification. The carbon, hydrogen and nitrogen content were measured using CHN analyzer 1000 LECO in accordance with the ASTM D 5373 standard while, the total sulphur was measured using energy dispersive X-ray fluorescence analyzer (EDXRF ED 2000 Oxford) in accordance with ASTM D 4239 - Standard Test Method for Sulphur (ASTM D 4239-11, 2011; ASTM D 5373-08, 2008).

The jarosite waste was subjected to the TCLP test by putting them in contact with distillate water for 24 h (1day). The pH (5) of the solution was kept constant with the addition of acetic acid (US EPA, 1993).

2.3. Mineralogical and Morphological characterization

Mineralogical composition of the jarosite tailing waste samples was determined by powder X-ray diffraction (XRD6000 Shimadzu). The microstructure, morphology, surface texture and elemental composition of jarosite waste samples were analyzed using scanning electron microscope (SEM) (TESCAN 5136 MM) equipped with energy dispersive X-Ray spectrometer (EDS). The feature analyses were estimated using Oxford/EDS software.

2.4. Thermogravimetric analysis (TG)–differential thermal analysis (DTA)

Simultaneous thermo gravimetric (TG) and differential thermal analysis (DTA) were performed on NETZSCH STA 449 apparatus. Differential thermal analysis (DTA) was used to determine endothermic and exothermic heat effects accompanying physical and/or chemical changes of the sample.

3. Results and discussions

The total metal content of jarosite waste in Kosovo obtained by ICP-OES is shown in Table 1. As can be seen from Table 1, iron in the form of Fe₂O₃ has the highest content (44.82 %) among all other elements. SiO₂ is also an important component with 6.29%. Therefore, the average values were used here to describe the characteristic of total metal content in jarosite waste. As a whole, the total levels of Zn and Pb were much higher than the concentration of Cu, Cd, Ni, Mn and As. Lower levels of elements such as Co, Cr, Ba, Sr and Ag were recorded as well. The results showed the presence of carbon with 0.56%, sulphur with 6.55%, hydrogen 0.77%, nitrogen 0.48% and phosphorus 0.0073%. The EDX analysis further confirmed the presence of these elements. This is also supported by earlier published works (Kerolli-Mustafa, 2015). The jarosite wastes were subjected to US EPA TCLP tests to determine the element leaching concentration (Table 2). This test was applied to assess the degree of the hazardous nature of jarosite waste. The concentration of elements in the leachate of jarosite wastes were compared with Kosovo regulatory limits. US EPA TCLP tests confirm that the toxic elements leaching concentrations of zinc, lead and cadmium in jarosite waste are 5625.21 mg kg⁻¹, 131.54 mg kg⁻¹ and 58.67 mg kg⁻¹, respectively. These concentrations are higher than the regularity limits confirming their hazardous nature.

The results highlighted that Zn, S and Mn leachate concentrations were much higher than those of other elements. This is confirmed with the fast increase of element concentration eluate extracted after 1 day of

the leaching process. From all analyzed elements sulphur (S) showed the most obvious tendency in leaching. In general, the total concentrations of As and other heavy metals in jarosite waste were much higher than those evaluated by the leaching test. These results were consistent with those reported by Kim and Hesbach, 2009.

Table 1. Total metal content and elemental composition in jarosite waste samples.

Element	mean \pm σ
Al ₂ O ₃ , wt. %	1.44 \pm 0.02
Fe ₂ O ₃ , wt. %	44.82 \pm 0.04
SiO ₂ , wt. %	6.29 \pm 0.6
Zn, wt. %	10.15 \pm 0.02
Pb, wt. %	7.5 \pm 0.14
Cu, wt. %	0.93 \pm 0.01
Ag, mg kg ⁻¹	132.52 \pm 11.72
Ba, mg kg ⁻¹	566.70 \pm 183.53
Co, mg kg ⁻¹	28.28 \pm 0.25
Cd, mg kg ⁻¹	2203.69 \pm 22.27
Cr, mg kg ⁻¹	406.39 \pm 12.25
Mn, mg kg ⁻¹	6283.74 \pm 74.05
Ni, mg kg ⁻¹	91.40 \pm 1.06
Sr, mg kg ⁻¹	136.10 \pm 1.01
As, mg kg ⁻¹	5025.33 \pm 4.42
S, wt. %	6.55 \pm 0.02
C, wt. %	0.56 \pm 0.01
H, wt. %	0.77 \pm 0.01
N, wt. %	0.48 \pm 0.02
P, wt. %	0.0073 \pm 0.01

Leaching concentrations (mg kg⁻¹) of As was much lower than the leaching concentration of other heavy metals, which means that the leaching levels of As were presenting only meager proportions for the total arsenic content in the jarosite tailing. Kim *et al.* also reported a similar result on the leaching of As from mine tailings (Kim and Hesbach, 2009). In their study, As leaching levels were in the range of 0.0017–0.37%, when mine tailings were mixed with water for 1 hr at a ratio of 1:5 as mass. Even though the test conditions such as leaching solution and shaking time do not correspond to those in our study, the result also satisfies that soluble As in leachate occupied only a minor fraction of the total As in jarosite tailing (Lim *et al.*, 2009). We consider that the pH of each leachant presumably affected most greatly the As extraction reaction. As mobilization, was found to be high for low or elevated pH levels such as pH < 2 or pH > 8 (Kim and Hesbach, 2009; Lim *et al.*, 2009). High pH promotes solubilisation of As under reducing conditions (little or no free oxygen), whereas in neutral or acidic soils the risk of solubilisation is minimized (Kim and Hesbach, 2009; Lim *et al.*, 2009). Considering the pH values of our leaching conditions the As results showed to be stable and does not present any toxicity threats for the jarosite tailing. Therefore, the leaching of Zn, Pb and Cd should be closely monitored.

The major mineral phases of jarosite waste are: ammonium jarosite, (NH₄)Fe₃(SO₄)₂(OH)₆, franklinite, ZnFe₂O₄, quartz, SiO₂, anglesite PbSO₄, anhydrite CaSO₄, mikasaite Fe₂(SO₄)₃, magnetite Fe₃O₄ and hematite Fe₂O₃. The XRD patterns of original jarosite samples are shown in Figure 1.

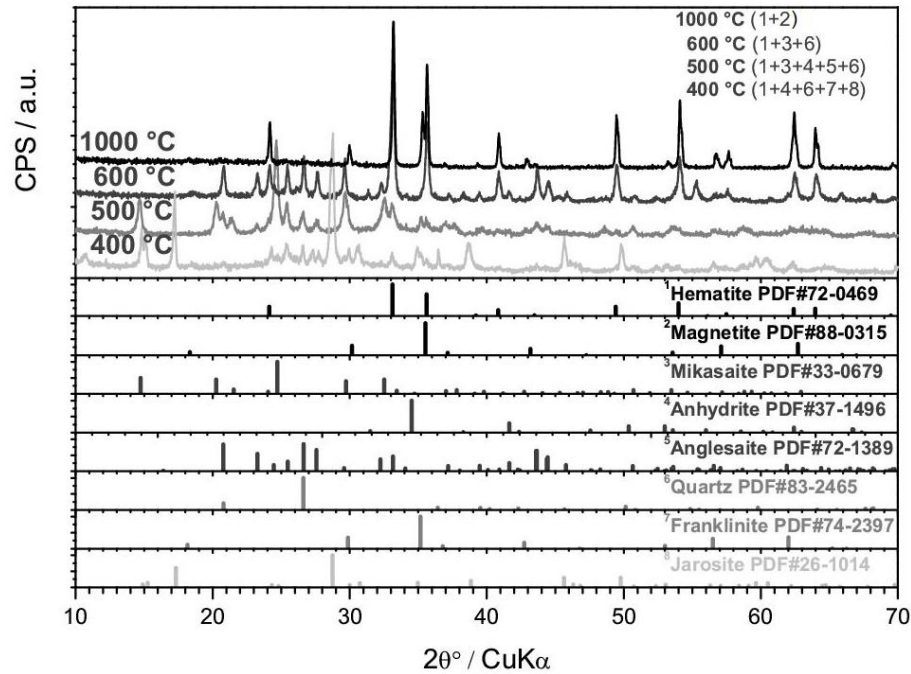


Figure 1. XRD pattern of jarosite waste

Table 2. Toxicity leaching characteristics of jarosite waste.

Element (mg kg^{-1})	t , day (Mean \pm σ)
Ag	0.13 \pm 0.07
Al	86.44 \pm 4.00
Ba	0.23 \pm 0.13
Cd	58.67 \pm 3.99
Co	0.77 \pm 0.02
Cr	0.06 \pm 0.04
Cu	59.89 \pm 3.57
Fe	28.04 \pm 9.67
Mn	383.70 \pm 31.48
Ni	2.81 \pm 0.77
P	1.63 \pm 0.36
Pb	131.54 \pm 5.79
S	9557.37 \pm 424.12
Si	35.82 \pm 0.57
Sr	12.61 \pm 0.18
Zn	5625.21 \pm 39.43
As	0.35 \pm 0.04

In order to determinate the thermal decomposition sequences of jarosite, samples were fired at temperatures up to 1000 °C in a laboratory muffle furnace. As expected, the calcinations temperature significantly affects both composition and structure of jarosite (Kerolli-Mustafa M. *et al.*, 2015). After heating at 700 °C, 900 °C and 1000 °C jarosite changed colour from reddish-brown to dark brown and consisted of hematite and magnetite, as shown by XRD analysis (Fig. 2). In our case, after temperature treatment of jarosite waste at 500 °C and 600 °C we could observe transient decomposition phases at 500 °C, as observed

with the disappearance of jarosite characteristic diffraction peaks, where the decomposition of jarosite is completed. XRD data of samples treated at 1000 °C yield the patterns of hematite and furthermore magnetite (Fe_3O_4).

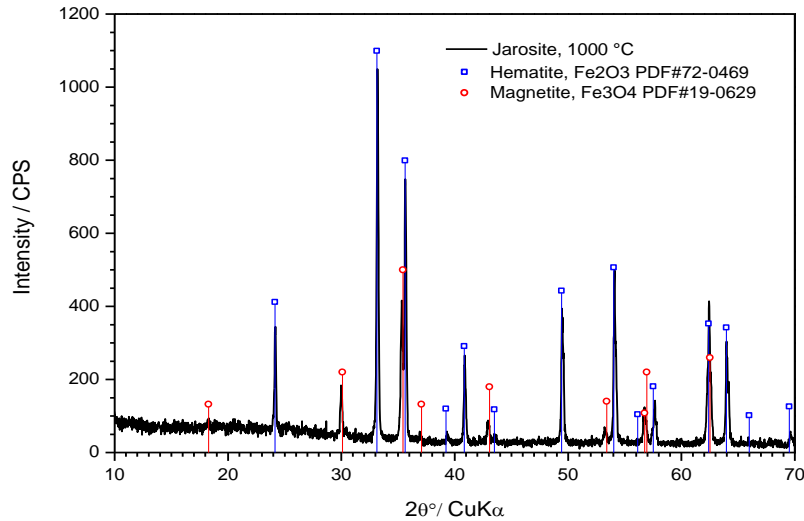


Figure 2. XRD patterns of jarosite decomposition.

The scanning electron microscopy (SEM) of jarosite waste indicates that jarosite samples have a micro crystalline morphology with no well-defined crystal form. All the investigated samples show similar morphology, primarily consisting of aggregates with non-uniform shape. The particle size of all jarosite samples are less than 500 μm , yet due to agglomerated particles and irregular amorphous particles the particles size distribution was occasionally broader. SEM images of the jarosite samples are shown in Figure 3. The EDS analysis further confirmed the presence of elements: Fe, S, Zn, Pb, Al, Si, O, C, Ca and As. This confirms that jarosite waste, beside Fe and S, contains various elements such as: Zn, Pb, Al, Si etc. (Kerolli-Mustafa *et al.*, 2015).

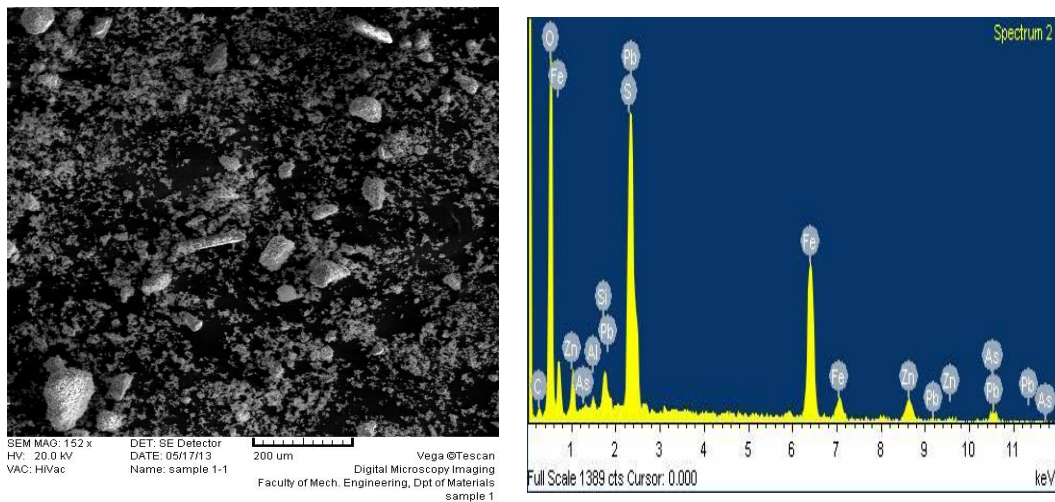


Figure 3. SEM images of jarosite waste samples

The SEM/EDS investigation (Fig. 3) confirms high intensities for jarosite elements (Fe, S, O) which support the findings of XRD analysis (Kerolli-Mustafa *et al.*, 2015). However the results of SEM/EDS demonstrate that the heavy metals do not exist alone.

TG/DTA thermograms for jarosite samples are shown in Figure 4 and it is possible to observe three distinct regions of weight loss. The total weight loss over the temperature range 25–500 °C is 10.8%. The first weight loss (1.87 %) occurs between room temperature and 100 °C and is attributed to the loss of adsorbed water. The second weight loss in the temperature range of 100 to 200 °C is attributed to the dehydroxylation of jarosite with the corresponding loss of H₂O. Between 200 °C and 430 °C a third weight loss of 6.89% occurs, which is attributed to the decomposition of jarosite. These results led to conclusion that jarosite structure is essentially preserved up to 400 °C. This is in line with the findings of XRD.

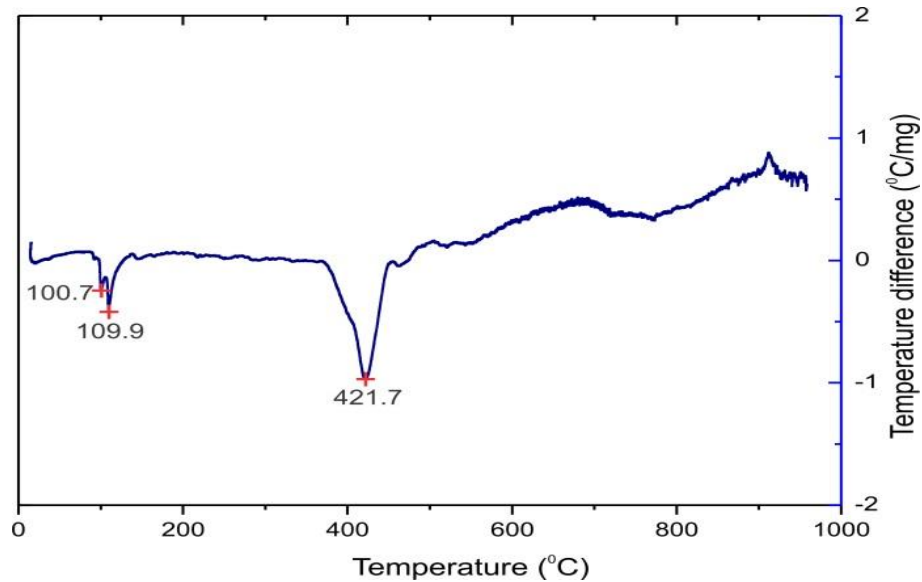


Figure 4. DTA curves of jarosite waste

The radioactivity levels in jarosite are below the limits specified from environmental point of view (Table 3).

Table 3: Radioactivity level of jarosite.

Radionuclides (Bq kg ⁻¹)	Concentration (ppm)
40 K (β emitters)	251.46 \pm 13.28
226 Ra (α emitters)	49.40 \pm 0.44
228 Ac (α emitters)	62.0 \pm 2.47

The values of naturally occurring radionuclide are as follow: 40K (251.46 Bq kg⁻¹), 226Ra (49.40 Bq kg⁻¹) and 228Ac (62 Bq kg⁻¹). The analysis using the XRD, SEM and TG, DTG and DTA techniques showed that jarosite waste is a potential resource that might be recycled in a technically feasible and environmentally friendly manner (Kerolli-Mustafa *et al.*, 2015). However, the jarosite waste can be incorporated as an additive with fine grained materials like clay and improve the quality of several building materials (Baciano, 2007; Kerolli-Mustafa *et al.*, 2015). The jarosite chemical characteristics showed that jarosite can be used effectively as an enriching medium for recycling and developing good quality building materials. Therefore, the strength reduction, volume reduction and detoxification/immobilization are the common practices for hazardous waste management. As well, the recovery of valuable materials and recycling them for making other products or applications is an interesting and essential aspect. The use of jarosite waste as a cementations materials/raw materials or additives could be realized in manufacturing blended cements, concrete, bricks

and aggregates. This would contribute to the control and reduction of release of pollutants to the environment. The jarosite characteristics show that jarosite waste is suitable for the production of glass ceramics. This process and the production of glass ceramic from jarosite waste in Kosovo are in process. In general, jarosite showed very good application possibilities such as a substitute for natural gypsum in cement production, production of stabilized/solidified products in construction (bricks, blocs, tiles and composites). Jarosite may also be reprocessed and iron as hematite can be obtained from it.

4. Conclusions

In the frame of sustainable development and waste management, the possible utilization of jarosite waste was of interest to be analysed. The study aimed to bring a series of contributions in very complex field of jarosite waste characterization and possible utilization. Extensive analyses of jarosite waste in Kosovo are applied through detailed characterization and leaching. The XRD and SEM studies confirmed the size and morphological behavior of jarosite waste, while the detailed thermal study confirmed that the jarosite structure preserved up to 400 °C. Also, the DTA technique was a vital benefit to find out the dehydroxylation of jarosite with the corresponding loss of H₂O. Thermal analyses evoke three distinct regions of jarosite weight loss over the temperature range 25–430 °C. The radioactivity levels in jarosite are below the limits specified from an environmental point of view. The physico-chemical characteristics of jarosite waste showed that there are application potentials of jarosite, which have to be recycled in environmentally friendly manner. Thus, converting hazardous jarosite waste into a non-hazardous material is of great importance for environmental, economical and social development. However, the production of cost effective materials from jarosite will show good market potentials and will significantly contribute to successful commercialization of innovative processes. These results needs to serve as a new opportunity and encouragement for entrepreneurs and construction agencies to develop new products and processes using jarosite wastes as raw materials for setting up secondary industries.

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