#### **REVIEW PAPER**

# FEASIBILITY STUDY OF INDUSTRIAL JAROSITE WASTE AS VITAL MATERIAL FOR CONSTRUCTION: POSITIVE AND NEGATIVE ASPECTS

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**Abstract:** Jarosite is a basic hydrous sulphate containing potassium and iron. Jarosite is often produced as a by-product during the purification and refining of zinc. The Jarosite mainly contains iron, sulphur, zinc, calcium, lead, cadmium and aluminium. The work presented here will overview the physical and chemical characteristics of Jarosite and as well as the work done by various authors. This paper will study the potential application of Jarosite in various engineering works such as road construction, airfields, dams, bricks and tiles. The text deals with various positive and negative aspects of using Jarosite for engineering purposes as Jarosite released from industrial process is complex and its quality and quantity make the task more complex for safe disposal. Due to the increasing of annual production of Jarosite, it is a major source of pollution for surrounding environment including soil, vegetation and aquatic life.

Keywords: Hazardous waste, Jarosite, concrete, zinc, fly ash, gypsum, corrosion

#### **1.0** Introduction

Concrete is one of the most durable building materials. It gains strength over time. Structures made of concrete can have a long service life. Concrete is used more than any other manmade material in the world. As of 2006, about 7.5 billion cubic meters of concrete are made each year, more than one cubic meter for every person on Earth. Jarosite is a waste material produced during extraction of zinc ore concentrate by hydrometallurgy operations (Asokan *et al.*, 2005&2008; Gregg, 2008). Its chemical formula is KFe<sup>3+</sup><sub>3</sub>(OH)  $_6(SO_4)_2$ . Zinc ore concentrate contains about 50 % zinc. This concentration is roasted at 900 °C and subjected to leaching where Jarosite is formed as a waste material. At present, the annual production of Jarosite is about 0.4 million metric tons while its accumulation is very less because it is converted into new material called Jarofix by addition of 2 % lime and 10 % cement (Sinha *et al.*, 2012 a & 2013a).

Universally, zinc industries are releasing huge quantity of Jarosite during zinc metal extraction process as solid residues. About 0.25 million tons per annum of Jarosite is released in India and due to the presence of toxic substances like zinc, lead, cadmium and other metallic and non-metallic oxides, which may cause chronic effects on environment or on human health. The Jarosite process of electrolytic refining of zinc is extended and improved by treating the Jarosite residues to recover valuable by-products. The wet Jarosite residue is acidified with sulphuric acid from the refining process acid plant to redissolve the iron sulphate, producing a liquid containing dissolved plant nutrients. Waste rock pikes with yellowish coatings of Jarosite are shown in Figure 1.

The economics of the process of zinc refining are very greatly enhanced by the recovery of valuable by-products from waste material and they can be useful in the refinery plant. In Indian industries, about 0.25 million tons per annum of Jarosite waste is being released. The European Union produces 0.60 million tons of such zinc residues every year. The major quantity of Jarosite is generated mainly from Spain, Holland, Canada, France, Australia, Yugoslavia, Korea, Mexico, Norway, Finland, Germany, Argentina, Belgium and Japan (Asokan *et al.*, 2006a and 2006b).



Figure 1: Waste-rock pikes with yellowish and greenish coatings of Jarosite at the Swansea mine site near silver city.

# 1.1 Properties of Jarosite

Jarosite has a trigonal crystal structure and is brittle, with basal cleavage, a hardness of 2.5-3.5, and a specific\_gravity of 3.15-3.26. It is translucent to opaque with a vitreous to dull lustre, and is dark yellow to yellowish-brown in colour. It is sometimes be confused with limonite or goethite with which it commonly occurs in the gossans (oxidized cap over an ore body). Jarosite is an iron analogue of the potassium aluminium sulphate and alunite. The general composition and properties of Jarosite can be referred to Tables 1 and 2.

ruble 1. Composition of Fullosite			
Pottasium	7.81 %		
Iron	33.45 %		
Hydrogen	1.21 %		
Sulphur	12.81 %		
Oxygen	44.73 %		

Table 1: Composition of Jarosite

Molecular weight of Jarosite = 500.81 gm.

Table 2: Physical	properties and	technical	parameters	of Jarosite
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Chemical formula	$\text{KFE}^{+++}(\text{SO}_4)_2(\text{OH})_6$
Empirical formula	$KFe^{3+}_{3}(SO_{4})_{2}(OH)_{6}$
IMA status	Valid Species (Pre-IMA) 1852
Locality	Barranco Jaroso in southern Spain.
Name origin	Named after its locality.
Lustre	Sub-Adamantine, Vitreous, and Resinous
Transparency	Translucent
Comment	Sub-adamantine to vitreous on crystal faces; resinous on fractures.
Colour	Amber-yellow, yellow-brown, to brown or light yellow.
Streak	Pale-yellow
Hardness	2 <sup>1</sup> / <sub>2</sub> - 3 <sup>1</sup> / <sub>2</sub> (Mohs)
Tenacity	Brittle
Cleavage	Distinct/Good Distinct on {0001}.
Fracture	Irregular/Uneven, Conchoidal
Density	$2.9 - 3.26 \text{ g/cm}^3$

## 1.2 Characteristics of Jarosite

Jarosite waste is a group of wide variety of particles ranging from clay to fine sand. The content of Jarosite is tabulated in Table 3. Particle size distribution is an index indicating

what sizes (particle size) of particles are present in what proportions in the sample particle group to be measured.

Table 5: Particle size distribution of Jarosne (Rathore et al., 2014)				
Particles	Content			
Silt sized	$63.48 \pm 0.19\%$			
Clay sized	$32.35\pm0.19\%$			

Table 3: Particle size distribution of Jarosite (Pathore at al. 2014)

#### 1.2.1 **Physico-Chemical Characteristics**

Physico-Chemical Characteristics is a method of investigating physicochemical systems that determines the nature of the interactions between the components of a system through a study of the relations between the system's physical properties and composition. The physico-chemical characteristic is shown in Table 3 as follows;

Table 4: Physico-chemical characteristics of Jarosite (Rathore et al., 2014)

Electrical conductivity	$13.26 \pm 0.437 \text{ dS/m}$
Humidity	44 to 47%
pH	2.6-4.0

#### 1.2.2 Chemical Composition

Chemical composition refers to the arrangement, type, and ratio of atoms in molecules of chemical substances. Chemical composition varies when chemicals are added or subtracted from a substance, when the ratio of substances changes, or when other chemical changes occur in chemicals. Rathore et al. (2014) has listed in detail the chemical composition of Jarosite (refer Table 5).

S.No	Parameters	Composition
1	SiO <sub>2</sub>	$6.75 \pm 0.412$
2	Al <sub>2</sub> O <sub>3</sub>	$6.75 \pm 0.152$
3	MgO	$1.86\pm0.067$
4	$Fe_2O_3$	$32.12 \pm 0.436$
5	CaO	$6.87\pm0.151$
6	ZnO	$9.18\pm0.175$
7	Na <sub>2</sub> O	$0.61 \pm 0.424$
8	K <sub>2</sub> O	$0.74 \pm 0.023$
9	PbO	$1.95 \pm 0.132$
10	SO <sub>3</sub>	$31.19 \pm 0.246$

Table 5: Chemical composition of Jarosite (Rathore *et al.* 2014)

## 2.0 Literature Review

Jarosite compound is associated with sulphide minerals. So, due to its acidic conditions and heavy metal content, Jarosite can be used as a proxy in remote-sensing studies to locate the area of high acidity and metal leachability, thereby providing a rapid and efficient way to screen mined areas for potential sources of acidic drainage. Jarofix is a stable material obtained by mixing Jarosite with 2% lime and 10% cement and have the great potential to be utilized for the construction of road embankment (Havanagi *et al.*, 2012). While the other significant mix like Jarofix-soil mix (50-75%) and Jarofixbottom ash mix (50-75%) can also be utilized for the construction of embankment and may be used for construction of sub-grade layer of road pavement (Sinha *et al.* 2012b & 2013b). The Physico-chemical characteristics of Jarosite indicate that there is a good utilization potential of Jarosite-sand mixture in building materials like bricks, cement, tiles, and composites.

### 2.1 Review of Experiments on Jarosite

Little work has been done on Jarosite waste yet. But experiments reveal that when Jarosite is mix with Portland cement, it increases the strength and other vital properties up to a significant amount (Mymrin *et al.*, 2005). The work by Mymrin *et al.* (1999) reported that new materials result from mixtures of Jarosite waste, dump ferrous slag and Al-surface cleaning waste with or without small addition of Portland cement possesses good strength and water resistance. These characteristics make them highly recommendable for use as construction materials for road and airfield runways, levee cores, industrial dumps, and multi-storey building foundations, in tile and brick production thereby saving the total construction cost.

The possibility of replacing the natural gypsum, used in cement production, by a Jarosite/alunite chemical precipitate was investigated. For this purpose, nine mixtures were produced by substituting gypsum, from 0% to 100%, by the Jarosite/alunite precipitate. All samples were tested by determining the setting time, compressive strength, grindabality and content of water soluble chromium. Furthermore, XRD analysis was used to determine the hydration products after 2, 7, 28 and 90 days (Katsioti *et al.*, 2005).

The compressive strength of concrete was checked by replacing sand with Jarosite in the following percentages: 0%, 20%, 40%, 60%, 80%, and 100%, respectively in concrete mixes. The concrete was prepared in the ratio of 1:2:4 and Jarosite waste was obtained from Hindustan Zinc Limited (HZL). OPC was used as binder in cement concrete mixes in this work (Vyas *et al.*, 2011). The Unconfined compressive strength (UCS) test was measured using universal testing machine and results are tabulated in Table 6.

S.No	Cement	Fine aggregate		Coarse	Total	UCS (28
	(opc) kg	Sand (kg)	Jarosite (kg)	aggregate (kg)	weight (kg)	days in kg/cm <sup>2</sup> )
1	1.0	2.00	0.00	4.0	7.00	170
2	1.0	1.60	0.40	4.0	7.00	155
3	1.0	1.20	0.80	4.0	7.00	140
4	1.0	0.80	1.20	4.0	7.00	125
5	1.0	0.40	1.60	4.0	7.00	100
6	1.0	0.00	2.00	4.0	7.00	65

Table 6: Unconfined Compressive Strength of Concrete by Replacing Sand with Jarosite (Vyas *et al.* 2011)

Research has been done on solidified Jarosite-sintered products. Their engineering properties such as density, shrinkage, water absorption capacity and compressive strength were examined. In each case, triplicate samples were tested and average values were reported. The compressive strength was tested using Shimadzu SERVOPULSER Material Testing Machine (Compressive Testing Machine) Model EHF-EG 200 KN-40L, Japan. The rate of pressure applied was 27.27 kg/cm<sup>2</sup>/min till the brick break and the break point was measured for compressive strength (Asokan *et al.*, 2007).

Study of the effect of Jarosite clay ratio and fly ash on density of s/s-sintered products has been done by Kalwa and Grylicki (1983). Results revealed that the density of fired bricks developed from different ratios of Jarosite and clay ratio along with 0–45% fly ash resulted to 1.4–1.93 g/cm<sup>3</sup>. Different experimental trials showed that the density of fired bricks had increased when the Jarosite clay ratio increased. However, when fly ash was applied more than 15%, the density of Jarosite bricks decreased with increasing Jarosite. The minimum density was recorded with maximum fly ash addition wherein Jarosite clay ratio was 4:1 (Asokan *et al.*, 2007).

The idea of substituting natural gypsum by the Jarosite precipitate in order to produce Portland cement was also studied. It was based on the high sulphate content of the mineralogical phases and the need to find an industrial use for this by-product. Besides, it is assessed that the cost of using the Jarosite/alunite precipitate would be lower than that of quarrying, grinding, and transporting of natural gypsum (Katsioti *et al.*, 2005). Replacement of natural gypsum by non-calcium sulphate salts was investigated and studies found out that the non-calcium cations affected the rheological properties of cements pastes. More specifically, the sulphates of zinc, iron, potassium and sodium decreased both the plasticity and the setting time of the cement pastes. It has also been found that the presence of  $Cr^{3+}$  retards the setting time (Bombled, 1980). In the work reported by Katsioti *et al.*, a series of runs was conducted to produce the Jarosite/alunite precipitate from real laterite heap leach liquor by precipitation, at atmospheric pressure, to be used as a substitute of gypsum in cement production. Nine different mixtures were

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produced with 95% clinker content, by replacing gypsum, from 0% to 100%, with Jarosite/alunite precipitate and the grindabality index of each mixture was determined. All nine mixtures were tested for setting time, compressive strength, grindabality and water-soluble chromium, in order to determine optimum percentage of substitution. Furthermore, all samples were analyzed for water soluble  $Cr^{6+}$  by treating the solid cement with water (w/c = 10), at ambient temperature, for 15 min. Liquors samples was subsequently reacted with biphenyl carbizide in acid solution to produce a pink colour. The setting times of cement samples were determined using the European Standard. Compressive strengths at 2, 7 and 28 days were also measured (Katsioti *et al.*, 2005).

No. of samples	% Clinker	% Gypsum	% Jarosite	% Substitution of Gypsum from Jarosite
1	95.00	5.00	0.00	0
2	95.00	4.75	0.25	5
3	95.00	4.50	0.50	10
4	95.00	4.25	0.75	15
5	95.00	4.00	1.00	20
6	95.00	3.75	1.25	25
7	95.00	2.50	2.50	50
8	95.00	1.25	3.75	75
9	95.00	0.00	5.00	100

Table 7: Composition of samples (Katsioti et al., 2005)

Table 8: R	lesults of	grindabality	v test (	Katsioti et	al., 2005)
		0 2			

No. of sample	Mill revolutions	Specific surface	Grindabality index	Specific gravity (gm/cm2)	Water soluble Cr <sup>6+</sup> (ppm)
1	4200	3945	0.94	3.15	75
2	4275	3950	0.92	3.15	77
3	4400	3950	0.90	3.15	67
4	4400	3970	0.90	3.15	68
5	4300	3960	0.92	3.14	65
6	4150	3970	0.96	3.15	41
7	3900	3970	1.02	3.15	43
8	3700	3965	1.07	3.15	30
9	3750	3985	1.06	3.16	14

Table 9: Determination of setting time (Katslott <i>et al.</i> , 2005)					
No. of sample Initial time		Final time (min.)	Water of normal		
	( <b>min.</b> )		consistency (%)		
1	145	225	23.2		
2	145	220	23.2		
3	155	215	23.4		
4	150	205	23.7		
5	150	215	23.6		
6	90	165	24.6		
7	60	105	25.6		
8	20	32	36		
9	15	35	35		

Table 9: Determination of setting time (Katsioti et al., 2005)

Table 10: Results of compressive strength (Katsioti et al., 2005)

No. of sample	% SO3	Strength (Mpa) 2 days	Strength (Mpa) 7 days	Strength (Mpa) 28 days
1	2.75	27.1	37.7	48.1
2	2.69	24.3	37.7	44.2
3	2.63	25.1	36.6	44.4
4	2.56	25.1	37.7	44.5
5	2.50	24.0	36.5	44.4
6	2.44	23.3	34.7	44.2
7	2.13	19.4	34.1	41.67
8	1.81	0.6	2.3	39.26
9	1.99	0.7	3.0	31.40

Grindabality index of each sample was determined and is presented in Table 8. The grindabality index reaches its maximum values when 75% and 100% of gypsum is substituted by the Jarosite/alunite. The precipitate, which is an easily grind able material, results in an increase of the grindabality index of the mixtures produced. The samples were analyzed for water soluble  $Cr^{6+}$  and the corresponding values are, also, given in Table 8. The water-soluble chromium ( $Cr^{6+}$ ) appeared to decrease as the quantity of gypsum, replaced by the Jarosite/alunite precipitate, increased. As can be shown in Table 8, the reference mixture, that had been produced by 95% clinker and 5% gypsum (sample 1), presented a  $Cr^{6+}$  value of 75 ppm, as the result of  $Cr^{3+}$  oxidation, contained in the raw meal, under the oxidizing conditions in the rotary kiln. On the contrary, the  $Cr^{6+}$  value of sample 9, produced by total replacement of gypsum with Jarosite/alunite, was determined at 14 ppm.

The setting times of the cement mixtures are given in Table 9. As shown, the increase of the Jarosite/alunite substitution in the cement mixtures results in lower setting times. This can be attributed to the decrease of the water soluble  $SO^3$ , present in Jarosite/alunite precipitate compared to the natural gypsum. Furthermore, as was mentioned before, the presence of Fe<sup>3+</sup> and Cr<sup>3+</sup> ions in the Jarosite/alunite precipitate instead of Ca<sup>2+</sup> in the natural gypsum, can lead to a higher decrease in plasticity and shortening of setting time. This decrease reached its highest levels at 75% and 100% of gypsum replacement, where the "flash set" phenomenon was observed because of lack of sufficient Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions. Consequently, it was impossible to control initial hydration of the aluminate phase (C<sub>3</sub>A).

The compressive strengths at 2, 7 and 28 days, as well as the % SO<sub>3</sub> content, were also determined and the results are given in Table 10. At the age of 2 days, there is a slight decrease in the strength value, while at the age of 7 days the changes are not significant, in comparison with the reference mixture (sample 1: 95% clinker and 5% gypsum). However, in the case of 25% and 50% replacement, at the age of 28 days, a decrease, ranging from 4 to 6 MPa, was acknowledged. Moreover, at the replacement levels of 75% and 100%, the rate of the hydration reaction appeared to be decreasing, resulting in lower compressive strengths (39.26 and 31.4 MPa, respectively). The retarding of the compressive strength could be attributed to the shortening of setting time because of the decrease in water soluble SO<sub>3</sub> and the increase of  $Cr^{3+}$  in the mixtures with Jarosite/alunite.

The fact that the grindabality index, setting time and compressive strengths were similar to those obtained with the mixture with no Jarosite/alunite addition (sample 1), lead to the conclusion that the optimum mixture was the one, in which 20% (sample 5) of the gypsum had been replaced by the Jarosite/alunite precipitate as shown in figure 2. X-Ray Diffraction Analysis (XRD) investigates crystalline material structure, including atomic arrangement, crystallite size and imperfections.



Figure 2: X-ray diffraction of sample 5 (20% gypsum substitution) at 7, 28 and 90 days (M. Katsioti *et al.*, 2005).

Jarosite is effectively used in making bricks of good strength. It is mixed with some other additives like fly ash, clay so as to obtain the optimum workability. Asokan *et al.* (2006a) also studied the ratio of different matrixes used in developing Jarosite bricks. The details of different matrixes ratios and water consumption for making solidified products are shown in table no. 11. The composite matrix was mixed well till it became a homogenous workable state.

Trials	Jarosite - clay ratio	Jarosi -te (gm.)	Clay (gm.)	Jarosite -clay weight (gm.)	Fly ash (gm.)	Fly ash %	Total weight (gm.)	Water binder ratio
1	1:1	500	500	1000	Nil	Nil	1000	0.242
2	1:1	425	425	800	150	15	1000	0.227
3	1:1	350	350	700	300	30	1000	0.210
4	1:1	275	275	550	450	45	1000	0.195

Table 11: Experimental details and quantity of different matrixes used in developing Jarosite bricks (Asokan *et al.*, 2006a)

Although Jarosite has many *positive effects* on concrete and bricks and improve some of their properties but in a case study, it was observed that deterioration of concrete was due the formation of Jarosite. The deteoriation of concrete surface due to the expansion

by the formation of Jarosite was studied in 1990. The presence of Jarosite as a corrosion product in concrete has been observed only scarcely. A case study of the corrosion phenomena in a Belgian bridge reveals the formation of Jarosite, caused by the oxidation of a rare type of aggregate, consisting essentially of two minerals: quartz and pyrite. In a first survey examination, some of the yellowish powder out of the pop-out cores is sampled. Later on, four cores are drilled. These are oriented perpendicular to pop-out zones in different stages of their evolution. The yellow powder is examined by means of the X-ray diffraction (XRD) equipment.

The yellowish reaction product, sampled at the concrete surface in the core of a pop out, can be determined by means of XRD as a mix of three minerals: quartz (SiO<sub>2</sub>), gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) and Jarosite (KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>). The remarkable yellowish colour of the powder is due to the predominant presence of the potassium-iron sulphate mineral Jarosite (L. De Ceukelaire, 1991).

### 2.2 Negative Effect of Jarosite

#### 2.2.1 Corrosion Process

The formation of the reaction products the porous, pyritic black "sandstone" is an easy prey for the process of oxidation. Especially in the surface layer of the concrete, where the rinsing and penetrating rain water creates an ideal environment, the risk of corrosion is very high. Along with the air, present in the concrete or penetrating through the surface layer, the water supply can cause a rapid corrosion of the pyrite. The chemically basic nature of the pore solution in the concrete even supports the oxidation process, as it consists mainly of potassium and sodium hydroxides. Schematically, the first step in this corrosion process of pyrite can be written as follows:

$$2FeS_2 + 2O_2 + 7H_2O \implies 2FeSO_4 + 2H_2SO_4$$
(1)

The ferrosulphate (FeSO<sub>4</sub>) however, is unstable in a basic environment, and as the sulphuric acid in reaction is neutralized, this iron compound will react (in the presence of more water and oxygen) to form the ferrisulphate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). As the pore solution of concrete is very alkaline (pH: 12.5 to 13.7), the produced sulphuric acid will get little opportunity to create an acid environment wherein the ferrosulphate is stable. Consequence, this acid compound is neutralized quickly by the reactions [2a], [2b] and [2c] with the hydroxides of the pore solution. In fact, the sulphates of potassium and sodium can be formed at first, but these salts are more soluble than calcium sulphate. Hence, the latter will be the end product, in spite of the fact that the concentration of calcium ions in solution is not that high. The presence of calcium in the solid phase is abundant, however, and through chemical processes of equilibrium, this source of calcium can be used to form more calcium sulphate than the initial calcium ion concentration in the pore solution may seem to permit.

$$H_2SO_4 + 2 \text{ KOH} \longrightarrow K_2SO_4 + 2 H_20$$
 (2a)

$$H_2SO_4 + 2 NaOH --> Na_2SO_4 + 2 H_20$$
 (2b)

$$H2SO4 + Ca(OH)_2 --> CaSO_4.2H_2O$$
(2c)

The red-ox reaction, responsible for the transition from ferrosulphate to ferrisulphate, can be given by the expression:

$$12 \text{ FeSO}_4 + 302 + 6 \text{ H}_2\text{O} \longrightarrow 4 \text{ Fe}_2 (\text{SO}_4)_3 + 4 \text{ Fe} (\text{OH})_3$$
 (2d)

After the transition of  $Fe^{2+}$  ions to  $Fe^{3+}$  ions, the formation of the compound Fe(OH3) from Fe3+ ions does not occur in a direct way, but step by step. The hydrated Fe3+ ion (Fe<sup>3+</sup>.6H<sub>2</sub>0) is the initial reaction product of the redox-reaction, and this reacts as an acid, by releasing protons in three stages (reactions [3a, 3b and 3c]).

$$Fe^{3+.}6H_2O --> Fe^{3+}(OH).5H_2O + H^+$$
 (3a)

$$Fe^{3+}(OH).5H_2O --> Fe^{3+}[(OH)]_2.4H_2O + H^+$$
 (3b)

$$\operatorname{Fe}^{3+} [(OH)]_2.4H_2O \longrightarrow \operatorname{Fe}^{3+} [(OH)^{-3}.3H_2O + H^{+}$$
 (3c)

After the second proton release [3b], and before the final third step [3c] towards the formation of Fe(OH)3, the ion Fe3+[(OH)]2 is created. This ion fits extremely well in the formula of Jarosite (KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>), that can be written as  $K^{+}$  { Fe<sup>3+</sup>[(OH)]<sub>2</sub> }<sup>3</sup> (SO<sub>4</sub>)<sub>2</sub>.

This explains the affinity to the formation of the little soluble compound Jarosite when potassium and sulphate ions are in the neighbourhood. The sulphate ions have their origin in the soluble salts  $K_2SO_4$  or  $Na_2SO_4$  (from the reactions [2a] or [2b]). Some sulphate ions can possibly be supplied by  $H_2SO_4$  that was not neutralized directly. When the solubility of Jarosite is smaller than that of gypsum, it is even possible that  $SO_4^{2-}$  ions of this latter compound can be used to build up the Jarosite structure.

So, the final reaction products are gypsum, Jarosite and ferric hydroxide. It is no coincidence that exactly these compounds are found in and around the pop-outs in the bridge piers. Gypsum and Jarosite can be detected by means of X-ray diffraction because of their crystallinity. The ferric hydroxide (as an amorphous phase not detectable by XRD) causes the rusty discoloration, spread all over the concrete surface by the washing rain. And indeed, the results of the microscopically investigations confirm these theoretical deductions.

## 2.3 The Deterioration Mechanism

The deterioration mechanism in the case of the pop-outs in the bridge piers is not of this kind. The occurrence of an expansion cannot be denied, but this increase of volume is related to the massive formation of gypsum and Jarosite in the boundary zone between the black "sandstone" aggregate and the cement paste in the concrete surface layer. The rust products are present too, but there are two reasons why they cannot be responsible for the expansion damage. Firstly, a portion of the Fe<sup>3+</sup> ions are built in the Jarosite structure. This means a reduction of the potential rust formation. Secondly, the expansive rust products are formed in the porous structure of the black "sandstone". So, the increase of volume can be compensated easily within the reactive aggregate itself. When the ferric hydroxides finally migrate through the cement paste to the concrete surface, they have lost their expansive force, because the volume changes occurred long before the migration stage.

The gypsum and the Jarosite formation takes place in or near the cement paste, because this reaction needs calcium or potassium ions. Consequently, disruption forces can be developed as these minerals are precipitated out of the pore solution of the concrete, and an expansion pressure will lead to the pop-out phenomena. One feature of this corrosion process still needs to be explained. Before a pop-out is developed completely, the first sign of the deterioration process is the brownish staining of the concrete surface as a prediction of more serious damage. Examination reveals that spots with rust stains always seem to be located just above a maturing pop-out.

The origin of the ferric hydroxide in these rust stains can be primary (out of the oxidation of the pyrite) or secondary (out of the possible disintegration of Jarosite). This secondary formation of ferric hydroxide can be expressed as a hydrolization:

 $KFe^{3}(SO_{4})_{2}(OH)_{6} + 3 H_{2}O - > K^{+} + 2(SO_{4})_{2} + 3Fe(OH)_{3} + 3H^{+}$  (4)

In either way, the ferric hydroxide is more mobile than the "insoluble" Jarosite, and can penetrate through the first cracks that are produced by the Jarosite or gypsum ruled expansion.



Figure 3: Detail of the stained bridge pier concrete popup (Ceukelaire, 1991).

### 3.0 Conclusions

Jarosite is a resource of great potential, which has to be recycled in a technically feasible and environmentally friendly manner. Thus, converting hazardous Jarosite into a nonhazardous material is of great significance. Its utilization will lead to saving of clay soil and other natural resources like fine aggregates used in developing building materials. From the review of research work carried out by number of authors, it reveals that compressive strength of Jarosite products, water binder ratio and water absorption capacity is quite good, the toxic elements and shrinkage were under the safe limits which conclude that Jarosite has the potential to be use in construction applications specially in embankment construction will certainly create value addition in the form of avoiding accumulation of waste on fertile land. The presence of Jarosite as a corrosion product in concrete is a very rare phenomena. The outcome of the study is expected to result in as one of the major solutions for safely and economically using the hazardous Jarosite released from zinc industries as blending Jarosite with concrete improves all major properties like compressive strength, grindabality index, consistency, durability and its cost benefit ratio is also good.

### 4.0 Acknowledgement

I would like to thank Prof. Meeta Verma, Prof. Sarah Khan, Prof. Sakshi Gupta, and Dr. D.K Singh for their valuable discussions on Jarosite waste from zinc industires.

#### References

- Asokan, P., Saxena, M., and Asolekar, S. (2005). *Coal combustion residues environmental implications and recycling potentials*. Resource conservation recycling 43:239-252.
- Asokan, P., Saxena, M., and Asolekar, S. (2006a). Hazardous Jarosite use in developing non hazardous product for engineering application. Journal of hazardous materials 137:1589-1599.
- Asokan, P., Saxena, M., and Asolekar, S. (2006b). *Jarosite characteristics and its utilization potentials*. Science of the total environment 359:232-243.
- Asokan, P., Saxena, M., and Asolekar, S. (2007). Solid waste generation in India and their recycling potential in building materials. Building and environment 42: 2311-2320.
- Asokan, P., Saxena, M., and Asolekar, S. (2008). Application of coal combustion residues and marble processing residues for immobilizing and recycling of hazardous Jarosite waste. Proceedings of the international conference on waste technology: 1290-1298.
- Ceukelaire L. D. (1991). Concrete surface deterioration due to the expansion by the formation of *Jarosite*. Cement and concrete research 21:563-574.
- Bombled J.P. (1980). *Influence of sulphates on the rheological behaviour of cement pastes and on their evolution*. In proceedings of 7<sup>th</sup> international congress on the chemistry of cement, Paris 3:164-169.
- Gregg A. Swayze, George A., Kathleen S., Heather A., Jane M., Sharon F., Reinhard W., and Rhonda L. (2008). *Chapter B: Understanding Jarosite from mine to mars.* U.S Geological survey circular no. 1328:96.
- Havanagi, V.G., Sinha, A.K., Arora, V.K., and Mathur, S. (2012). Waste materials for construction of road embankment and pavement layers. International journal of environmental engineering research 1:51-59.
- Kalwa, M., Grylicki, M. (1983). Utilization of fly ash, a waste from thermal power stations, in manufacture of building materials. Ceramic powders 5:107-109.
- Katsioti, M., Boura, P., Agatzini, S., Tsakiridis, P., Oustadakis, P. (2005). *Use of Jarosite/alunite precipitates as a substitute for gypsum in Portland cement*. Cement and concrete composites 27:3-9.
- Mymrin, A.V., Ponte, H.A., and Impinnisi, P.R. (2005). *Potential application of acid Jarosite* wastes as the main component of construction materials. Construction and building materials 19:141-146.
- Mymrin, A.V. and Vaamonde, V.A. (1999). *Technical note: New construction materials from Spanish Jarosite processing waste*. Mineral engineering 12:1399-1402.
- Rathore, N., Patilb, M.P. and Dohare, D. (2014). *Utilization of Jarosite generated from lead-zinc smelter for various applications*. International journal of civil engineering and technology 5:192-200.
- Sinha, A.K., Havanagi, V.G., Arora, V.K., and Mathur, S. (2012a). *Design, construction and evaluation of Jarofix embankment and sub grade layers*. International journal of environmental engineering research 1:97-103.
- Sinha, A.K., Havanagi, V.G., Arora, V.K., Ranjan, A. and Mathur, S. (2012b). *Recycling Jarofix waste as a construction material for embankment and sub grade*. The journal of solid waste technology and management 38:169-181.
- Sinha, A.K., Havanagi, V.G., Ranjan, A., Mathur, S. and Singh, B.K. (2013b). *Geotechnical characterization of Jarosite waste material for road construction*. Proceedings of Indian geotechnical conference: 22-24.

- Sinha, A.K., Havanagi, V.G., Arora, V.K., Ranjan, A. and Mathur, S. (2013a). *Characterization of Jarofix waste material for the construction of road*. Proceedings of Indian geotechnical conference: 35-43.
- Vyas, A.K. (2011). Solidification-stabilization technique for metal bearing solid waste from zinc industry- A case study. International conference on environmental and computer science 19:151-155.