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Recycling of Jarosite For Recovery of Valuable Metals and its Utilisation

[a] Manorama Swain, [b]K K Sahu, [c]B N Roy
[a]M.Tech student, BIT Sindri, Dhanbad ,India
[b]Principal Scientst, National Metallurgical Laboratory, Jamshedpur, India
[c]Assistant professor , BIT Sindri, Dhanbad, India

ABSTRACT: *About, 80% of world's total zinc is produced through conventional hydro-metallurgical process i.e. Roast-leach-electrolysis (RLE) process. . The process rejects iron in the form of jarosite, a crystalline and easily filterable solid residue. jarosite contains higher concentration of toxic elements like lead, zinc, sulfur, cadmium, chromium and copper etc. Due to these characteristics, jarosite itself is cosidered highly hazardous material universally and has detrimental effects on environment as well as human health. Jarosite residue collected from HZL is treated to recover different metal values. As such jarosite is a very stable matrix and all the metals present in it is in insoluble form. Direct dissolution of different metals from jarosite matrix was found very poor. Therefore, a combined sulfation–roasting–leaching process was developed for selective and quantitative dissolution and recovery. Sulphuric acid roasting followed by water leaching could recover Zn, Cd and other minor base metals quantitatively. The lead enriched in residue is recovered by leaching in brine solution of suitable composition. Finally AAS & XRD analysis is done for characterisation of materials. From the analysis, we conclude that after second stage brine leaching process recovery of zinc 98.58% , cadmium 99.99%, lead 99.92% and iron 86.34%.*

KEYWORDS: *Hazardous jarosite ,Valuable metal recovery, water leaching, brine leaching.*
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I. INRODUCTION

During hydrometallurgical extraction and purification of Zinc sulphide ore , huge amount of jarosite is released universially as solid residues. The process rejects iron in the form of jarosite, a crystalline and easily filterable solid residue. The major portion of jarosite consists of oxides of iron, sulphur and zinc. Most of the impurities present in the leach solution are also incorporated in to the matrix of Jarosite. Thus jarosite contains higher concentration of toxic elements like lead, zinc, sulfur, cadmium, chromium and copper etc. Due to these characteristics, jarosite itself is cosidered highly hazardous material universally and has detrimental effects on environment as well as human health.

Therefore the residue is usually dumped in the designated sites following proper guidelines**.** Safe dumping of the residue not only occupies costly agricultural lands but also incurred huge cost. Even with safe dumping, in long run due to weathering /bacterial action there is a release of toxic elements in soluble form which ultimately contaminate the soil, ground water and aquatic life. Thus safe dumping of the jarosite residue may not be a good option to take care of the environment. In this regard an attempt has been made in the present study to develop an environmentally friendly process to provide a workable solution for safely treating of hazardous jarosite waste with simultaneous recovery of all the valuable and toxic metals present in it.

In India,Hindustan Zinc Limited (HZL) has a multi-unit mining and smelting establishment having installed capacities of 3.49 million tonnes per year Zinc manufacturing from four smelters located in the states of Rajasthan, Andhra Pradesh, Bihar . Debari Zinc Smelter plant is one of the largest units having ammonium Jarosite process of Electrolytic extraction method. The current Zinc production capacity of HZL is 9,30,000 tonnes per annum and about 5 lakh matric tonnes Jarosite is realesed per annum.The jarosite is acidic in nature and PH is less than 3.5.
There are several techniques that have been developed world wide by several researchers for remediation of hazardous waste containing priority toxic elements.Solidification/stabilisation (s/s) process is one of the techniques,now commonly used to inhibit the transport of heavy pollutant elements into the surrounding environment and offers impoveement in the physical characteristics that reduce the leachablity of toxic metals.
Rusen et al. developed a process of acid leaching and brine leaching to reclaim Zn and Pb, respectively. About 71.9% Zn and 98.9% Pb can be recovered. [1] Turan et al. Developed a process of H_2SO_4blending, roasting,

water leaching, and finally NaCl leaching to recover Zn and Pb, respectively. About 86% Zn, 89% Pb can be extracted from the residue. These studies had not showed how to recover Cd and Cu presented in the waste.
Leaching of gold ,silver and lead from plumbo-jarosite containing hematite in HCl-$CaCl_2$ media is also studied by some researchers[2]
Shaohua 2011Ju developed a process for recovery of Pb, Cu, Ag and Cd from jarosite by using NH_4Cl leaching around 93% of each metals recovered. [3]

There is a possibility of using jarosite as a substitute for natural gypsum in cement production [4].

Jarosite waste can be detoxified through immobilization by making composite products using other inorganic industrial wastes as additives which are causing major environmental problems. Coal Combustion Residues (CCRs), Pond Coal Combustion Residues (PCCRs) and Marble Processing Residues (MPRs) can be used as additives along with clay using solidification / stabilization (s/s) and sintering process [4, 5].
The physico-chemical characteristics of jarosite indicates that there is a utilization potential of jarosite-sand mixture as building materials like bricks, blocs, cement, tiles, composites [6].
Development of alternative and lightweight building blocks for the substitute to the existing fired clay bricks [7].
Jarosite may also be reprocessed and iron as hematite can be obtained from it [8].
The physico-chemical characteristics of jarosite indicates that there is a utilization potential of jarosite-sand mixture as building materials like bricks, blocs, cement, tiles, compositesJarofix, a stable material obtained by mixing jarosite with 2% lime and 10% cement, itself have the potential to be utilized for the construction of road embankment. While jarofix-soil mix (50-75%) and jarofix-bottom ash mix (50-75%) have the potential to be utilized for the construction of embankment and may be used for construction of sub-grade layer of road pavement [9-14]

Jarosite seems to be a potential resource which has to be recycled in a technically feasible and environment friendly manner. The main objective of this project is

- Recovery of all valuable metals from jarosite.
- Reducing the toxic effect of jarosite before its disposal to the environment by recovering of toxic metals from jarosite.
- Development of a suitable process for recovery of metals from jarosite.

II. Materials and methods

2.1 Sample collection and processing

Jarosite samples were collected from the existing dump yard outside the plant area at Debari, Hindustan Zinc Limited, Rajasthan, India. The material was observed to be fine grained, light weight and resemble conventional soils .The samples were air-dried, sieved through 2mm size and stored in glass container. For characterisation sampling was done from the air-dried sample adopting conning and quartering method.

2.2 Chemical and mineralogical characterisation

Before the characterisation of materials dry acid digestion method was performed. For dry acid digestion 0.5g of jarosite sample was taken in a beaker. Then the sample was treated with HCl, HNO_3 and perchloric acid separately. Then the digested sample was filtrated and diluted for chemical analysis by atomic absorption spectrometer .The qualitative analysis of jarosite has been carried out by AAS. The phases in the original jarosite sample were analysed by XRD.

2.3 Instruments used for characterisation of the sample

The microscopic analysis of the sample were carried out by Scanning Electron Microscope. The chemical characterisation of the samples were carried out by atomic absorption spectrometer. The phases were analysed by X-ray diffraction spectrometer were 2-theta value is 90º.

III. EXPERIMENTAL DETAILS

3.1 Preliminary acid leaching study

Initially, HNO_3 and malic acid leaching of jarosite sample were studied to provide reference results. All the preliminary leaching experiments were carried out in flasks that were magnetically stirred using 10% pulp density where concentration of acid was (20-60gpl), roasting temperature (200°C–750°C) and leaching temperature 70°C for a period of 4 hours. After leaching, the leach residue were washed with distilled water and the solution was taken for AAS analysis.

3.2 Roasting of jarosite residue-H_2SO_4 mixture

An appropriate amount of H_2SO_4 was mixed with 100g of jarosite sample in a porcelain dish and placed in a Muffle furnace preheated to the required temperature. At the end of the predetermined heating period, the sample was removed from the furnace, cooled in a desiceator, weighted, ground and preserved in closed vessels to await analysis.

The effects of various parameters such as roasting temperature (200 - 750ºC), roasting time (120min), H_2SO_4/jarosite ratio (0.1 – 0. 3) on the roasting of the samples were examined.

3.3 Water leaching of jarosite residue-H_2SO_4 mixture

Prior to use, the roasting jarosite residue was leached with tap water at 40ºC for 60 min at 10% pulp density with mechanical stirrer at 600 rpm to improve the recovery in the subsequent stage of chloride leaching. After filtration, the solution was analyzed by atomic absorption spectrometer for zinc ,lead and iron. The residue was dried, ground, sieved, and physically characterized to determine the particle size distribution. Then the residue was chemically analyzed for zinc, iron, and lead using an atomic absorption spectrometer, and its mineralogical structure was identified by X-ray diffraction analysis.

3.4 Leaching for Lead Extraction

After water leaching, the jarosite residue was subjected to chloride leaching to recover lead. Commercial grade salt (NaCl), as a cheap agent, was used to prepare brine solution. Industrial grade HCl was used for pH adjustment.

The effects of NaCl concentration (220g/l), water leach residue around 10% pulp density, leaching temperature at 80°C and leaching time for 60 min and stirring speed 700 rpm were investigated. After brine leaching the brine leach residue was once again subjected to brine leaching so that lead could be thoroughly segregated from the jarosite residue. The leach liquor of both the brine leaching was taken for AAS analysis and leach residue for XRD analysis.

IV. RESULTS AND DISCUSSION

4.1 Chemical and mineralogical characterisation

The major portion of jarosite consists of oxides of iron, lead and Zinc chemical analysis of original jarosite as shown Table 4.1. The major mineral phases of the jarosite are potassium iron sulphate hydroxide $KFe_3(SO_4)_2(OH)_6$ and quartz (SiO_2). The phases in the original jarosite sample were analysed by XRD as shown in the Fig.4.1 below.

Table 4.1: Chemical analysis of original Jarosite sample

Sl No	Formula	Concentrtion(%)
1	Fe_2O_3	38.10
2	SO_3	27.02
3	SiO_2	12.26
4	ZnO	9.11%
5	PbO	8.23
6	Al_2O_3	3.07
7	K_2O	0.70
8	MnO	0.46

9	CaO	0.24
10	CuO	0.23
11	MgO	0.16
12	TiO_2	0.13
13	P_2O_5	0.09
14	Cl	0.06
15	V_2O_5	0.04
16	Ag	0.04
17	CdO	0.03
18	Cr_2O_3	0.03
19	Rb_2O	89PPM

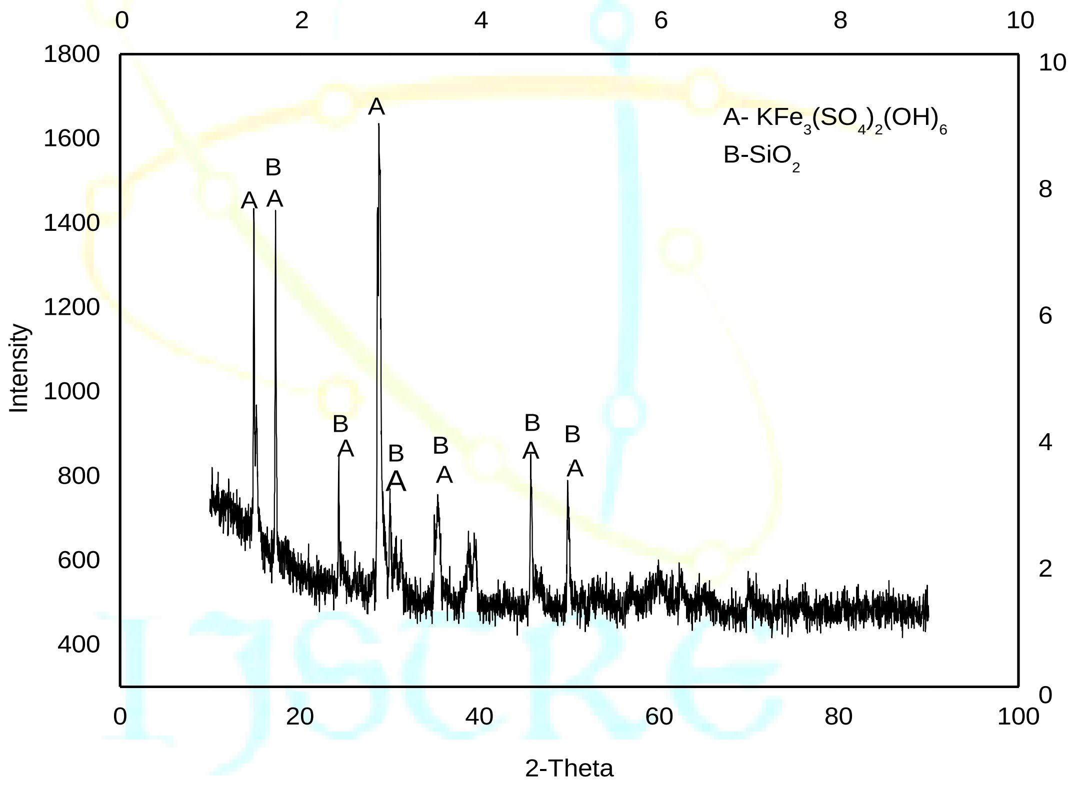


Fig. 4.1 XRD analysis of Original Jarosite Sample

4.2 Preliminary acid leaching study

Preliminary acid leaching study of jarosite sample were carried out using 10% pulp density, HNO_3 and malic acid (20-60gpl) respectively varying the roasting temperature (200-750ºC) for a duration of 4hrs. The AAS result of preliminary leaching experiments using 10% pulp density were tabulated in Table- 5.2 & Table-5.3 below**.**

Table .4.2 The AAS result of HNO_3 leaching experiments.

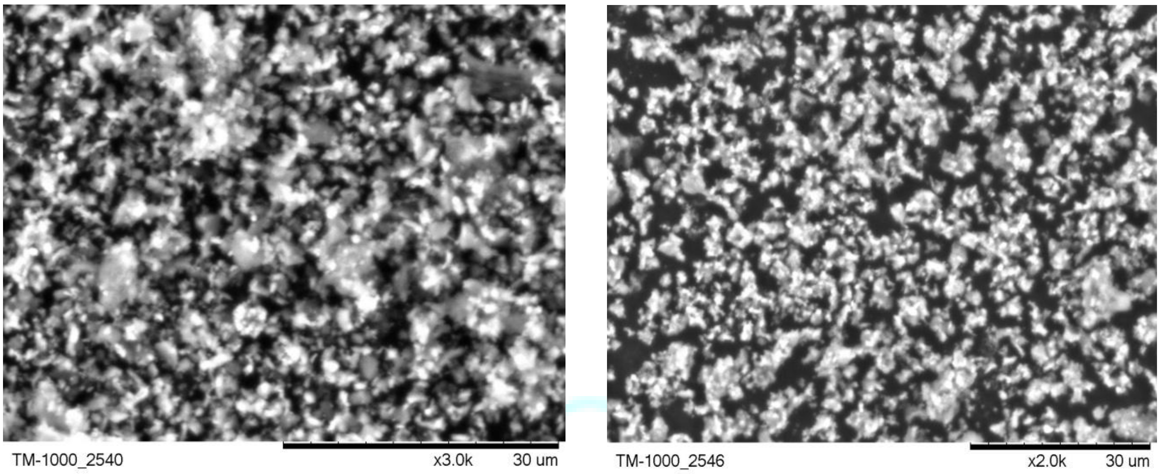
Sample Name	**%Pb**	**%Zn**
Original/HNO_3/60gpl	0.134%	2.276%
200°C/HNO_3/60gpl	0.237%	2.825%
400°C/HNO_3/60gpl	0.057%	3.343%
600°C/HNO_3/60gpl	0.0048%	4.838%
750°C/HNO_3/60gpl	1.06%	0.201%

Table .4.3 The AAS result of Malic acid leaching experiments.

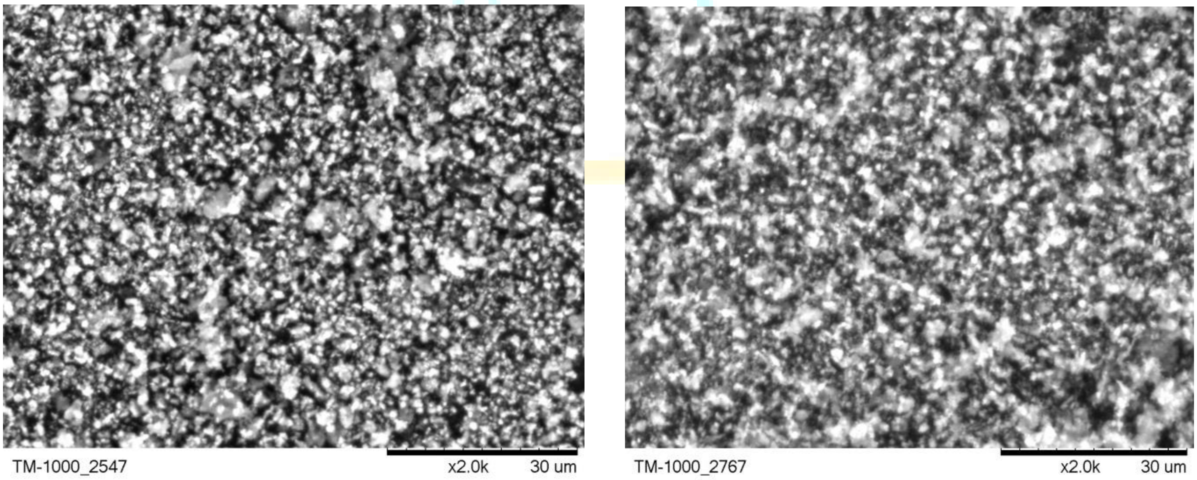
Sample Name	**%Pb**	**%Zn**
Original/Malic acid/60gpl	0.0141%	0.1856%
200°C/Malic acid/60gpl	0.0144%	1.784%
400°C/Malic acid/60gpl	0.0212%	1.653%
600°C/Malic acid/60gpl	0.021%	3.83%
750°C/Malic acid/60gpl	0.0093%	4.16%

The marginal dissolution of both zinc and lead was obtained under all the above condition with variation of either acid concentration or the roasting time. The maximum leaching of Zinc was obtained at 600ºC with acid concentration of 60gpl HNO_3 and 750ºC, 60gpl malic acid respectively as shown in the **Table -4.2 & Table-4. 3.** The effect of increasing temperature as well as acid concentration has no significant effect on the leaching of lead. Lead was not found in soluble form on increasing the concentration of either of the acids and further increase in roasting temperature.

As a result of these preliminary acid leaching studies, it can be concluded that lead and other associated metals could not be effectively leached from jarosite sample by using either HNO_3 or malic acid under above mentioned conditions.



(a) Jarosite without roasting **(b) At roasting temperature 400 ºC**



(c)At roasting temperature 600º C **(d) At roasting temperature 750º C**

Fig. 4.2: Microstructure of Jarosite roasted at different temperature.

Simple roasting of jarosite was done to see if dissolution of any specific metal selectively possible and also to see any change in characteristics of the sample. The roasting temperature was varied in the range 200ºC -750ºC. The microstructure of jarosite becomes finer with increasing roasting temperature **(Fig. 5.2).**

4.3 Roasting of jarosite-H_2SO_4 mixture

The sulfation-roasting-leaching process comprises three major steps : (1) Mixing the jarosite sample with sulphuric acid; (2) roasting and (3) water leaching. The sulphation roasting in the present study is carried out below and near the decomposition temperatures of the sulphates, when the following reactions takes place:

During H_2SO_4 mixing and the subsequent roasting stages, most of the oxides convert to their respective sulphates .Cited examples are given below:

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O \qquad (1)$$

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O \qquad (2)$$

$$Fe_2O_3 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 3H_2O \qquad (3)$$

$$ZnFe_2O_4 + 4H_2SO_4 \longrightarrow ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O \qquad (4)$$

At roasting temperatures of 600- 750ºC, sulphates with low thermal stability such as iron sulphate decompose to give their respective water – insoluble oxides.

$$Fe_2(SO_4)_3 \longleftrightarrow Fe_2O_3 + 3SO_3 \qquad (5)$$

4.4 Water leaching of jarosite -H_2SO_4 mixture

Jarosite residues are SO_4-bearing residues and the presence of excessive levels of sulfate adversely affects the lead extraction. In order to decompose the ferrite structure and to recover water soluble zinc such as $ZnSO_4$, a water leaching step has been found to be very effective. $ZnSO_4$ and $Fe_2(SO_4)_3$ are water soluble but $PbSO_4$ is water in soluble so during water leaching $ZnSO_4$ and $Fe_2(SO_4)_3$ come in to the solution and $PbSO_4$ remains in the residue.AAS analysis of water leached sample shows that zinc and iron are present in the solution but lead is completely absent. XRD analysis of water leached residue shows that $PbSO_4$ is present in the residue.

5.4.1 Effect of roasting temperature on leaching

Leaching experiments were carried out at 200 ºC, 400 ºC, 600 ºC, 650 ºC, 700 ºC and 750 ºC to investigate the effect of temperature on the dissolution behaviour of iron and Zinc. Samples were prepared with 0.3 mass ratio of Sulfuric acid) –to- (Jarosite residue). **Fig.4.3** shows the effect of roasting temperature on extraction of iron and Zinc. It is obvious that higher roasting temperatures will increase the decomposition kinetics of metal sulphates. The percentage of iron dissolution increases at 200ºC up to 600ºC. At 600 ºC percentage of iron dissolution is maximum which is around 77%. Further increase in temperature to 650 ºC, results in partial decomposition of iron sulphate to iron oxide. At roasting temperatures of 600 - 700ºC, sulphates with low thermal stability such as iron sulphate decompose to give their respective water – insoluble oxides .The water-soluble sulphates, on the other hand , are stable at such roasting temperatures and they dissolve easily during the subsequent water leaching step leaving the iron oxides in the residue. Iron and Zinc dissolution are lower when roasting is performed at 700ºC compared to dissolution after roasting at 650 ºC. By increasing the temperature from 650ºC to 750ºC , it is possible to decrease iron and Zinc dissolution from 28% to < 1% and from 98% to 40% respectively.

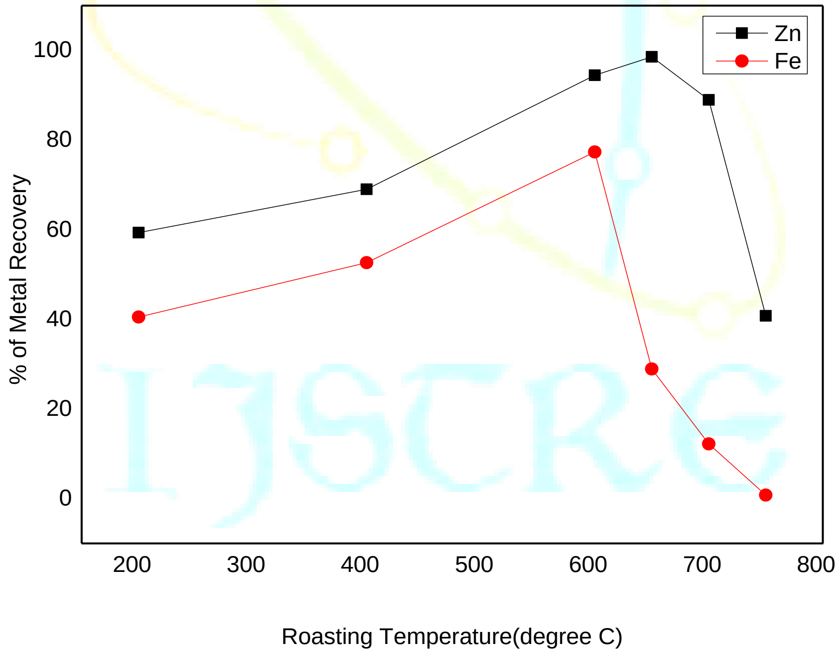


Fig.4.3 : Effect of variation of Roasting Temperature with same acid concentration on % of Metal Recovery

4.4.2 Effect of Acid Concentration on Leaching

A series of experiments were carried out by varying the mass of sulphuric acid to Jarosite residue from (0.1 – 0.3). The samples were roasted for 2hrs at fixed temperature of 600 ºC. After roasting , the samples was leached with water for 1 hr. Fig. Shows the dissolution of iron and Zinc at the roasting temperature of 600 ºC. At 600 ºC the percentage of dissolution of iron and Zinc increases with increasing acid concentration. Fig. Shows the dissolution of iron and Zinc at the roasting temperature of 750ºC.

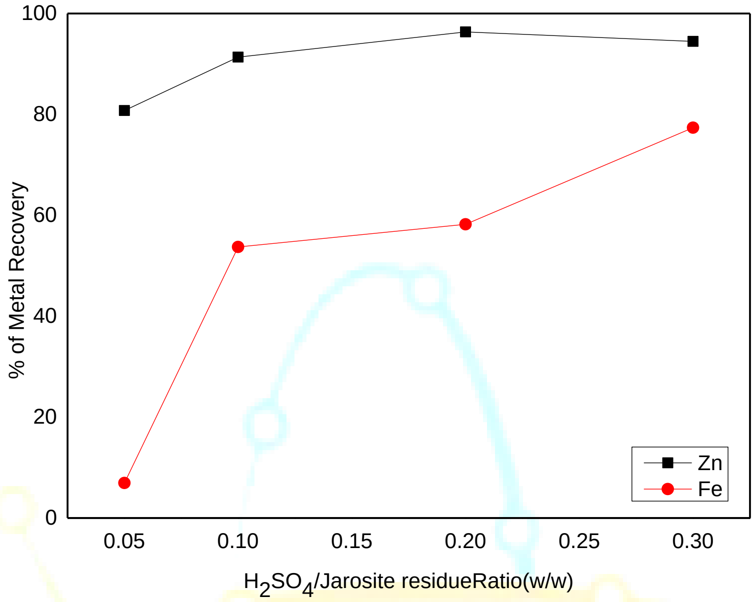


Fig.4.4 : Effect of variation of acid concentration on % of Metal Recovery at Roasting Temperature 600ºC

4.5 Brine Leaching follows water leaching for Lead Extraction

Brine leaching is based on the formation of complex chlorides of lead in concentrated chloride solutions. Lead sulfate is insoluble in water, but soluble in saturated chloride solutions acidified by HCl, H_2SO_4 or chlorine water.

$$PbSO_4 + 2\ NaCl \longrightarrow PbCl_2 + Na_2SO_4$$
$$PbCl_2 + 2\ HCl \longrightarrow H_2[PbCl_4]$$

In water lead sulfate has a low solubility ($Ksp = 10^{-8}$ at 25°C), compared to lead chloride which has moderate solubility. The saturated solubility of $PbC1_2$ in water is 9.9 g/L g at 20 °C and 33.4 g/L g at 100 °C. The $PbCl_2$ solubility decreases rapidly with increasing chloride concentration due to the so called common ion effect, but increases after passing through a minimum because the increasing chloride activity which favours the formation of soluble lead chloride complexes according to the following equations: [15]

$$PbCl^{2+} + Cl^- \longrightarrow PbCl^+ \quad k_1 = 12.59$$
$$PbCl^+ + Cl^- \longrightarrow PbCl_2 \quad k_2 = 14..45$$
$$PbCl_2 + Cl^- \longrightarrow PbCl_3^- \quad k_3 = 3.89 \text{ X } 10^{-1}$$
$$PbCl_3^- + Cl^- \longrightarrow PbCl_4 \quad k_4 = 8.82 \text{ X } 10^{-2}$$

After water leaching, the jarosite residue was subjected to brine leaching to recover lead. The effects of NaCl concentration (220g/l), water leach residue around 10% pulp density, leaching temperature at 80ºC and leaching time for 60 min and stirring speed 700 rpm were investigated. After first step brine leaching the percentage of recovery of Zinc and lead present in the residue as found in AAS analysis are shown in Table and Table respectively**.** The recovery of Zinc is almost 97% and the recovery of lead is around 99% after brine leaching**.**

Table-4.4 Recovery of Metals after brine leaching

Sl No	Treatment Condition	%Zn Recovery	%Pb Recovery	%Fe Recovery	%Cd Recovery
1	200ºC/30ml H_2SO_4	97.22	99.73	8.47	99.99
2	400ºC/30ml H_2SO_4	97.80	99.90	13.18	99.99
3	600ºC/10ml H_2SO_4	97.62	99.46	84.34	99.99
4	600ºC/20ml H_2SO_4	97.83	99.70	82.98	99.99
5	600ºC/30ml H_2SO_4	98.37	99.83	76.14	99.99
6	700ºC/30ml H_2SO_4	97.53	99.32	79.37	99.99
7	750ºC/10ml H_2SO_4	97.34	99.38	82. 44	99.99
8	750ºC/20ml H_2SO_4	97.32	99.61	82.67	99.99
9	750ºC/30ml H_2SO_4	94.66	99.88	82.75	99.99

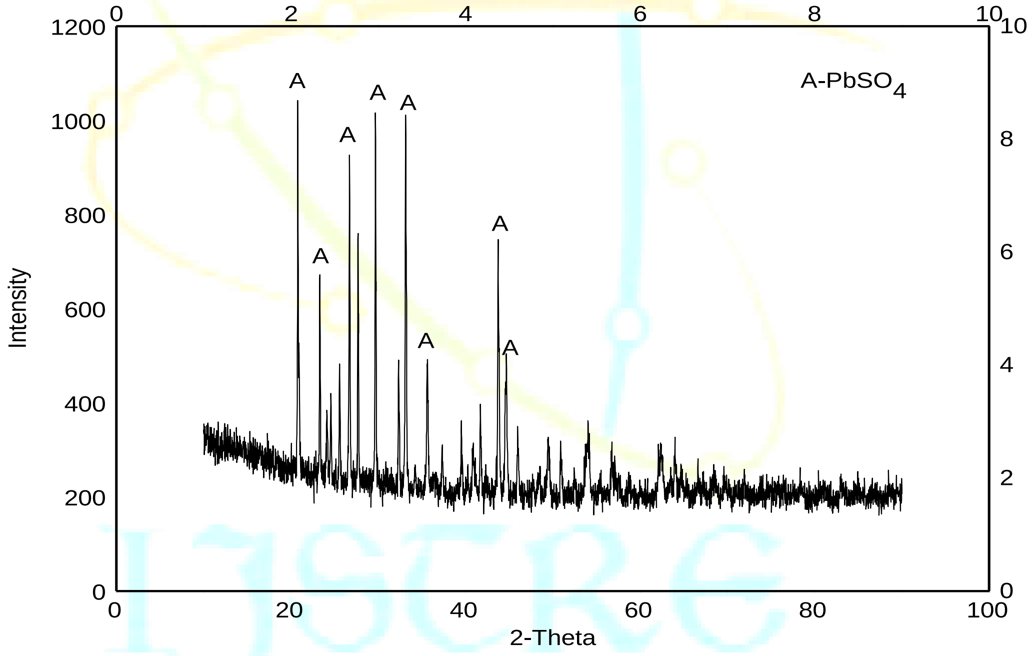


Fig.4.5 XRD analysis of acid roasted and water leached Jarosite residue at Roasting temperature 600 °C with acid concentration of 30% H_2SO_4

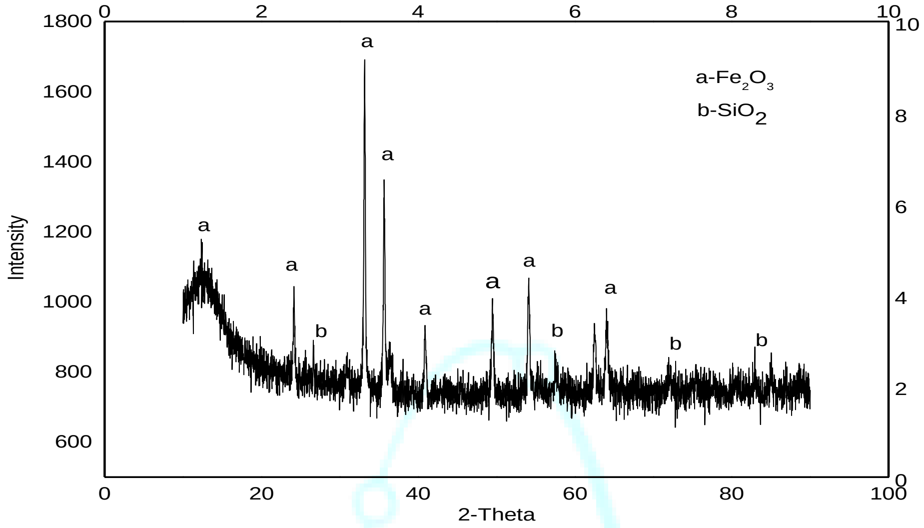
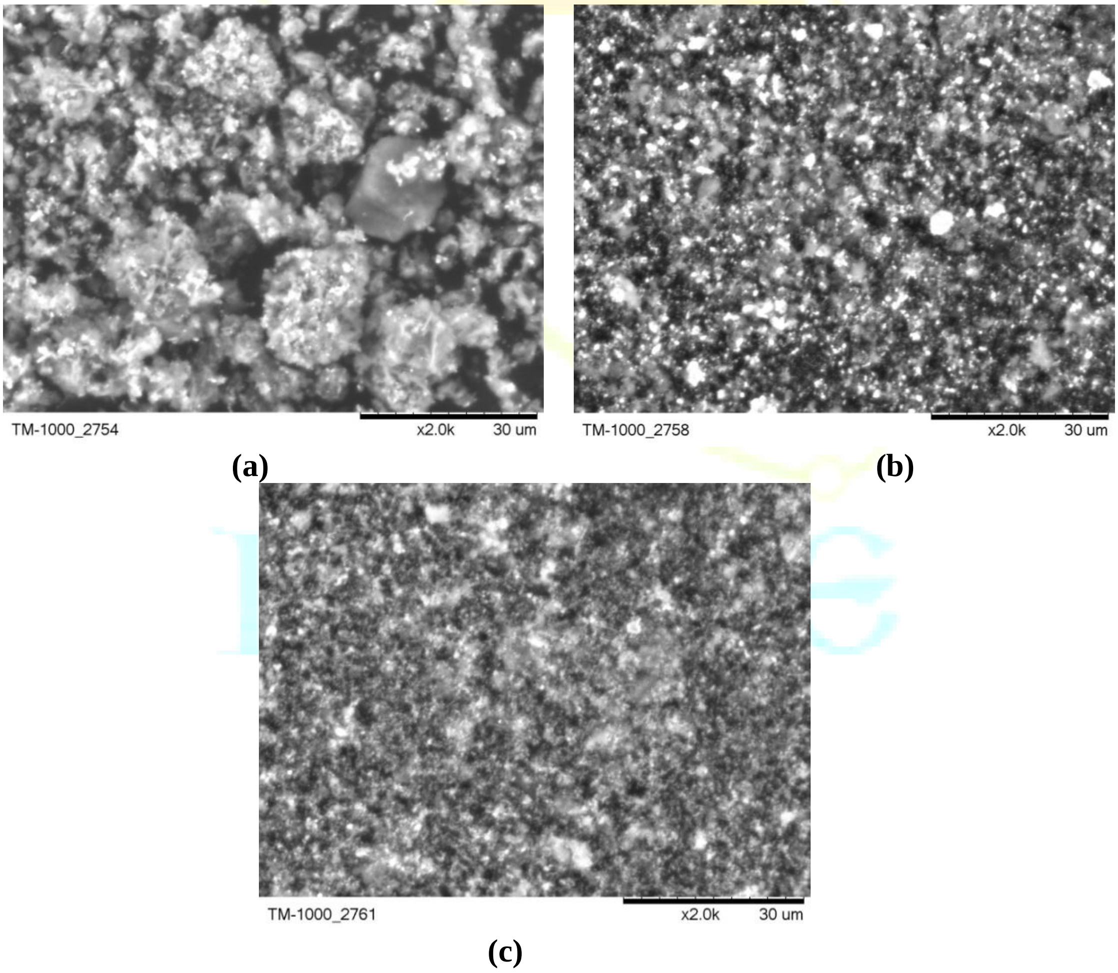


Fig .4.6 : XRD analysis of brine leached Jarosite residue at Roasting temperature 600°C with acid concentration of 30% H_2SO_4.



(a)

(b)

(c)

Fig(4.7a) : Microstructure of Acid roasted Jarosite with 30% Acid roasted at 600° C, **Fig(4.7b)** Microstructure of Acid roasted and water leached Jarosite residue. 30% Acid Roasting temperature 600ºC **Fig(4.7c) :** Microstructure of brine leached Jarosite residue. Roasting temperature 600 °C with acid concentration of 30% H_2SO_4 .

XRD analysis of acid roasted and water leached Jarosite residue at roasting temperature of 600°C and acid concentration of 30% H_2SO_4 shows that $PbSO_4$ is present in the residue . The microstructure shows that iron sulphate, Zinc sulphate and lead sulphate are present in the residue after roasting and after water leaching, water soluble iron sulphate and Zinc sulphate are leached and water insoluble lead sulphate is present in the residue.

XRD analysis of brine leached Jarosite residue at roasting temperature of 600°C and acid concentration of 30% H_2SO_4 shows that Fe_2O_3 and SiO_2 is present in the residue . The Microstructure of brine leached Jarosite residue at Roasting temperature 600 °C with acid concentration of 30% H_2SO_4 also shows that finer particles are present in the residue and these are Fe_2O_3 and SiO_2.

V. CONCLUSION

The recovery percentage of metals in first stage brine leaching is lead 99.83% Zn, 98.37%, Cd 99.99% and iron 82.75%.The recovery percentage of metals in second stage brine leaching is lead 99.92%, Zinc 98.58%, cadmium 99.99% and iron 86.34%. After brine leaching Jarosite is toxic free before its safe disposal to the environment and finally the bright red color residue comprising mainly Fe_2O_3 and SiO_2 can find market as pigment.

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