An Alternative Route for Valorization of Valuable Metals from Jarosite Residue

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This paper aims to consider the treatment of jarosite residue using a different reducing agents, aluminum, magnesium, and carbon. The jarosite residue is not standard – it contains higher amounts of Pb and Ag, as well as In, Ga and Ge. We show thermodynamical conditions of gas phase equilibrium for the given experiments and predominance diagrams that show potential for obtaining critical metals in the metallic phase. Using a mixture of aluminum and magnesium, as reducing agents, showed proper fuming of Zn and Pb at a temperature of 1200 °C. However, magnesium alone, and carbon in the mixture of reducing agents cause poor results for zinc fuming, which is explained by the modeling of the given compositions.

Key words: *jarosite residue, Indium, Gallium, Germanium, Zinc, metallothermic reactions*

1. INTRODUCTION

In the Zinc industry, the hydrometallurgical process is dominant for obtaining this metal: about 85% from the all World production [1, 2]. In the hydrometallurgical process for getting the Zinc metal, after acid leaching, zinc-ferric sludge as the byproduct is further treated in so-called jarosite procedure. In the jarosite procedure, Pb and Ag are valorized, and Fe is removed through the residue. Besides Fe, the other impurities are present in the jarosite residue (Zn, Cu, Ni, Cr, Co, As, Cd, Pb, Sb, Ge, Ga, In) and they could be mobile in the environment, causing the hazard consequences [3-10]. About 0.50 to 0.80 tonnes of jarosite is generated per tonne of zinc produced; six million tons per annum of jarosite residues are precipitated globally [8, 10].

Treatment of jarosite is mainly developed to prevent leaching of elements such as Cd, Pb, and As, like in the Jarofix process, where jarosite is mixed with Portland cement, lime and water, making chemically and physically stable material [10, 11]. For lower amounts of Zn and other metals, the pyrometallurgical route is not economically feasible [10]. In many cases, jarosite residue contains a significant amount of Zn, and other valuable metals like Ag, In, Ga, Ge Therefore, pyrometallurgical treatment methods are developed in order to utilize these metals. The most used method is the Waelz process [10]. The role of so-called critical technological metals like In, Ga, and Ge are of strategic importance for any country, and any source of these metals is precious.

The main goal of this paper is to show the possibility of using different reducing agents in the treatment of the jarosite residue with a significant amount of valuable metals. In Waelz process, using these alternative reducing agents could benefit in intensive fuming of Zn and Pb, optimizing energy consumption, and gathering metals such as Ag, In, Ga, Ge in the sponge iron.

2. EXPERIMENTAL WORK

The mixture was prepared using jarosite reside and powders of aluminum, magnesium and carbon. The commercial aluminum powder was obtained by air atomization in "Ecka granules – non-ferrous metals" Kranj, Slovenia. The purity of aluminum powder was 99.7%, with particle sizes -500 μm + 40 μm (mean 250

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μm). Magnesium powder was obtained from machining waste of magnesium alloy AZ63 from the factory „Magal“ Raška, Serbia, with particle sizes -500 μm + 40 μm (mean 250 μm). Nonstandard Jarosite residue originates from the factory „Zorka – non-ferrous metallurgy“, Šabac, Serbia. This residue is called Pb-Ag jarosite because it is rich on Pb and Ag.

Jarosite sludge samples were roasted to 850 °C to remove water and other volatiles. Roasted samples were mixed in different proportions of reducing agents: aluminum from 0 to 16.4 wt. %; magnesium from 0.0 to 13.9 wt. %; and carbon from 0.0 to 11.0 wt. % of the sample. The overall reducing agents amount was calculated to the equivalent amount of reducible oxides, with an excess coefficient of 1.15. Samples were pressed on the pressure of 40 bars, and then heated at 940 °C (samples 1, 2, 4, 5, 6, 7, 9), and 1200 °C (samples 3 and 8) for 20 minutes.

The chemical compositions of the jarosite residue and samples after treatment with the reducing agent were determined by the Atomic-Absorption Spectrophotometer (AAS), Perkin Elmer model ANALYST 300. Optical microscopy was done on Jenapol (Carl Zeiss, Jena, Germany) microscopy with the reflected light.

The thermodynamic HSC Chemistry Software v. 9.1 [11] was used for calculations and modeling of gas phases in the observed system, as well as for determination of In, Ga and Ge reduction conditions.

3. RESULTS AND DISCUSSION

The chemical composition of the jarosite sludge sample is given in table 1; loss of ignition (LOI) is mainly due to decomposition of NH_4^+, SO_4^{2-} and OH^- group, and evaporation of water (mean content of water is 3.2%).

Table 1. Chemical composition of Pb-Ag jarosite, wt. %

FeO	ZnO	PbO	SiO_2	S	CaO	MgO	Al_2O_3
42.00	10.40	7.52	7.35	8.64	1.52	0.04	1.59
MnO	P_2O_5	Cr_2O_3	TiO_2	Na_2O	K_2O	NiO	CuO
0.63	0.12	0.01	0.11	0.65	0.28	0.09	0.83
Co_3O_4	C	Ag	GeO_2	In_2O_3	Ga_2O_3	LOI	
0.03	0.42	0.02	0.018	0.020	0.011	<17.80	

The primary phase in the jarosite sludge is $NH_4Fe_3(SO_4)_2(OH)_6$. After roasting at 850°C, mass loss was about 30% due to the evaporation of volatiles; also, some amount of oxygen was reduced with sulphur. A mixture of roasted jarosite with different reducing agents and their amounts was heated at temperatures of 940 and 1200 °C. Mass balance is shown in Table 2. Note that all samples were held 20 minutes in the furnace, so kinetic of the process is not studied here, but the influence of the time parameter is significant, especially for the Waelz process.On the roasted jarosite sample, other phases can be observed: in Figure 1, marked as 1 (white) – galena PbS, 2 (yellow) – franklinite $ZnFe_2O_4$, 3 (grey) – magnetite Fe_3O_4, 4 (black) – silicates. The expected amounts of Zn and Pb after roasting are 11.90 % and 9.97%, respectively.

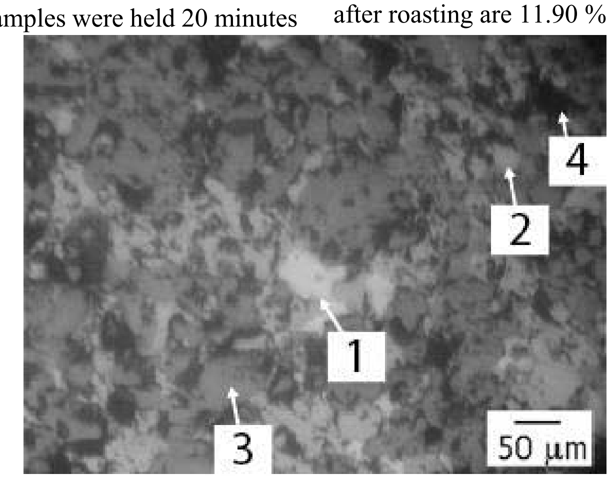


Figure 1 - Photograph of the jarosite sample obtained by optical microscopy

Table 2. Mass balance of treated jarosite sludge samples

	Sample	Mixture composition, wt. %				Reducing agent,%		
		Jarosite	Al	Mg	C	Al	Mg	C
Input	1	83.6	16.4	-	-	100	-	-
	2	84.2	8.2	7.5	-	50	50	-
	3 (1200 °C)	84.2	8.2	7.5	-	50	50	-
	4	92.5	-	7.5	-	-	50	-
	5	86.1	-	13.9	-	-	100	-
	6	84.3	5.7	5.3	4.7	35	35	30
	7	84.2	4.1	3.8	7.9	25	25	50
	8 (1200 °C)	84.2	4.1	3.8	7.9	25	25	50
	9	84.2	2.5	2.3	11.0	15	15	70

	Sample	Chemical composition, wt. %					Mass loss.%
		Fe	Zn	Pb	S	Mg	
Output	1	25.1	10.4	8.0	0.80	0.06	21.2
	2	30.6	7.6	2.1	1.52	6.5	31.5
	3	30.1	1.2	5.3	-	-	35.2
	4	33.3	11.3	8.5	1.27	6.6	37.9
	5	32.1	10.1	7.1	0.51	13.2	52.6
	6	32.3	10.1	9.1	0.56	4.49	27.0
	7	32.8	10.6	8.4	1.32	5.58	29.4
	8	35.2	8.9	6.2	-	-	32.5
	9	35.0	11.5	8.9	1.68	3.32	33.4

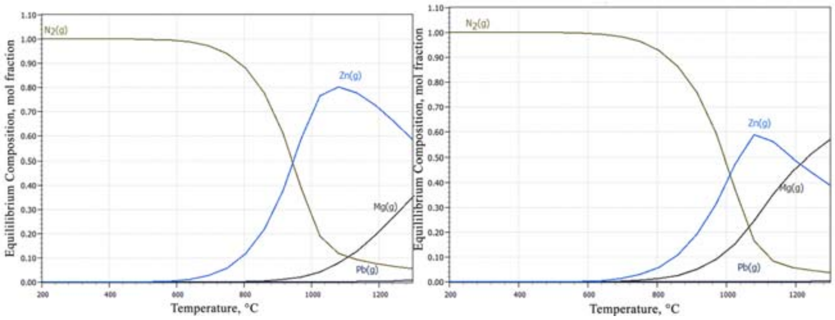
Magnesium alone (samples 4 and 5) shows a limitation in reducing of Zn and Pb oxides and only a small amount of magnesium was involved in the reaction at 940 °C. Using only aluminum as a reducing agent gives similar results (sample 1). Mixing of aluminum and magnesium in proportion of 50:50 (sample 2) reduces Zn and Pb oxides better than these reducing agents individually at the same temperature. At the temperature of 1200 °C (sample 3), it can be noted that a large fraction of Zn is reduced and evaporated from the sample. This is a proof that metallothermic reactions occur only after 1200 °C. The initiation of a metallothermic reaction depends on many variables. However, the metal particle size has the highest influence.

Using carbon in the mixture of reducing agents (samples 6 to 9) harms overall Zn and Pb removal, compared to the samples without carbon. Even on the temperature of 1200 °C, a small fraction of Zn and Pb was removed – better results were obtained using only mixture of aluminum and magnesium (sample 2) at 940 °C.

Observing the thermodynamical conditions, we could further discuss the results. In Figure 2, the equilibrium gas phase composition for samples 3 and 8 is presented. Using carbon as reducing agent is not favorable for reduction reactions, because CO(g) phase is absent in the gas phase; only solid carbon could involve in overall reactions with a tiny share, because of the slight contact between carbon and oxides. Even when the metallothermic reactions occur, zinc in sample 8 evaporates in smaller amount then in sample 3, because of the smaller amounts of Al and Mg.

Also, it can be seen in Figure 2 that Mg evaporates at 880 °C, together with Zn. Magnesium in the gas phase should amplify the reduction reactions with the oxides in the system. However, that is not the case in the given experiments. On the temperature of 1200 °C (sample 3 and 8), magnesium is not detected in the solid residue; obviously, magnesium evaporates without reacting with the oxides. This leads us to the conclusion that using magnesium as a reducing agent could be better if it is alloyed with aluminum, rather then alone.

In Al-Mg alloy, activity of aluminum decreases, which is favorable for aluminothermic reactions. At 940 °C, magnesium improves the reduction process when it is mixed with aluminum (comparison of samples 1 and 2). In the Waelz process, magnesium could react more intense, because contact between the gas and the solid phase is more intense in a rotary furnace.



a) b)

Figure 2 - .Equilibriumgas phase composition: a) sample 3, b) sample 8

The macrophotographs of the samples are given in Figure 3. Samples 2 and 3 had compact solid structure, and could be closest to the getting of sponge iron. This compact solid could contain valuable metals such as Ag, In, Ga, Ge and be further processed for their valorization

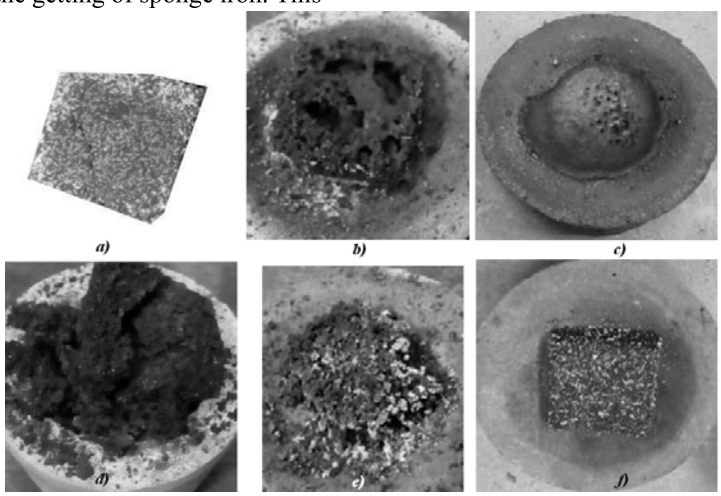


Figure 3 - Jarosite after treatment with different amounts of reducing agents, samples: a) 1, b) 2, c) 3, d) 4, e) 5, f) 8

Gibbs energies for the reduction of In, Ga and Ge oxides is given in Figure 4. As it was expected, the reactions with aluminum are the most probable. Also, all these reactions are highly exothermic, which is convenient and could intensify the Waelz process, optimizing energy consumption.

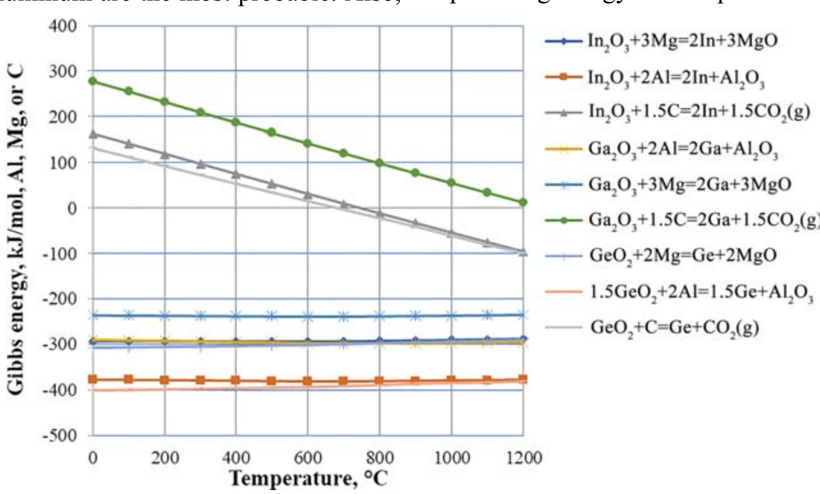
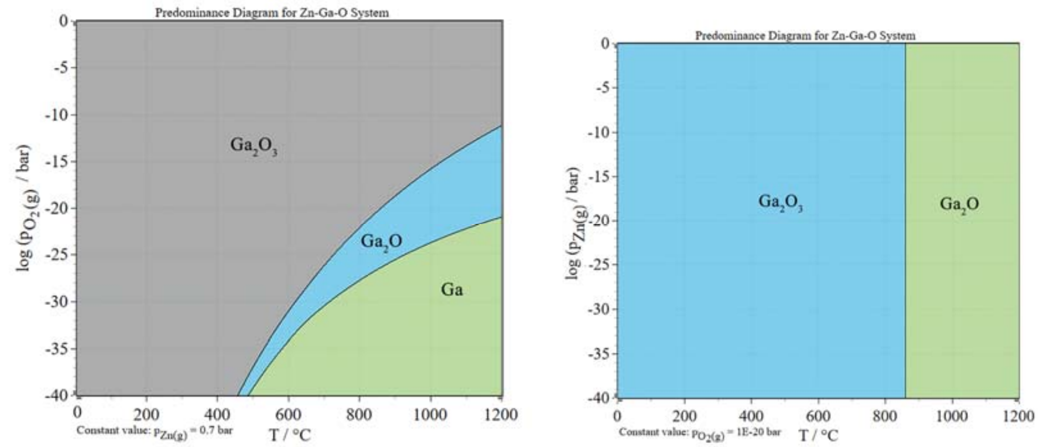


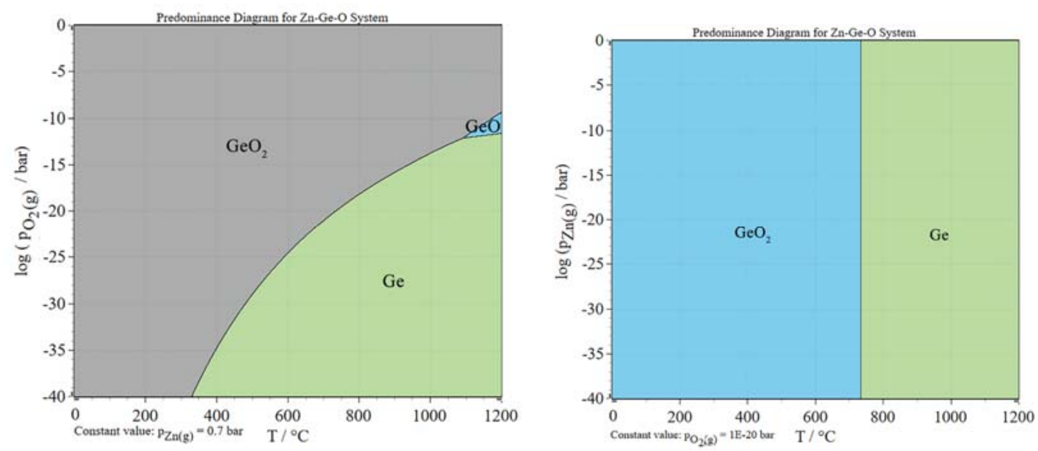
Figure 4 - Gibbs energy of possible reduction reactions in the system

Predominance diagrams for In and Ge show that, for a given condition (Figure 5, right sides), these metals will be in metallic phase at temperatures above about 780 °C.

On the left sides of Figure 5, it can be noted that partial pressure of oxygen in the system should be kept at low values to obtain In, Ga, and Ge in the metallic phase.



a)



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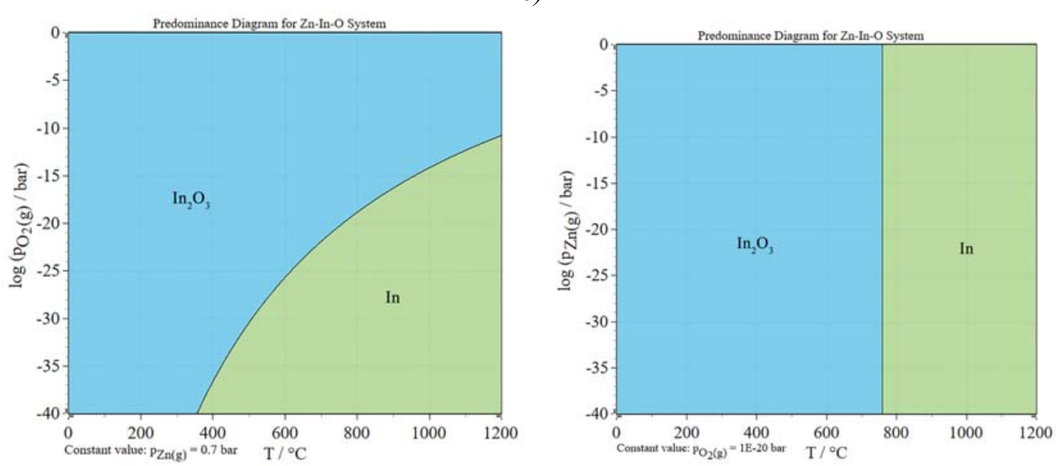

c)

Figure 5 - Predominance diagrams for a) Ga, b) Ge, and c) In, with a fixed amount of Zn = 0.7 bar – left side, and fixed amount of oxygen – right side

4. CONCLUSION

In the presented paper we show that it is possible to use the alternative pyrometallurgical route for the jarosite residue treatment. When a mixture of aluminum and magnesium is used as a reducing agent on 1200 °C, the large part of Zn and Pb evaporates. Thermodynamical modeling showed that In, Ga, and Ge are obtained as the metallic phase. Carbon addition in the mixture of reducing agent shows poor results compared to the samples without carbon. Further investigations should be directed to the industrial conditions conditions in a rotary furnace, with aluminum alloyed with magnesium - preferably from waste. In such a way, the synergy of materials is achieved and the materials cycle is more conserved.

5. ACKNOWLEDGMENT

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REZIME

ALTERNATIVNA METODA ZA VALORIZACIJU VREDNIH METALA IZ JAROSIT OSTATKA

U ovom radu prikazan je metod tretmana jarosit ostatka pomoću različitih reducenata: aluminijuma, magnezijum i ugljenika. Jarosit ostatak nije standardan – sadrži veće koilčine Pb i Ag, a pored njih i In, Ga i Ge. Prikazani su termodinamički uslovi ravnoteže gasne faze za date eksperimente, kao i uslovi u kojima će kritični metali biti sakupljeni u metalnoj fazi. Korišćenjem mešavine aluminijuma i magnezijuma kao reducenata postignuto je dobro isparavanje Zn i Pb na temperaturi od 1200 °C. Međutim, korišćenje samo magnezijuma ili ugljenika sa ostalim reducentima dovode do lošijih rezultata isparavanja cinka, što je objašnjeno modelovanjem datih sastava iz eksperimenata.

Ključne reči: *jarosit ostatak, indijum, galijum, germanijum, cink, metalotermijske reakcije*