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ON THE PHYSICOCHEMICAL PROBLEMS OF AQUEOUS OXIDATION OF POLYMETALLIC GOLD BEARING SULPHIDE ORE IN AN AUTOCLAVE

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The paper presents a study on the physical and chemical changes of iron, copper and zinc sulphide minerals in process of pressure oxidation. Oxidation in autoclave is a pre-treatment unit operation for refractory sulphide ores and concentrates in order to valorise gold, which is encapsulated mainly in pyrite matrix. Raw materials and solid residues are characterised. Basing on the results of chemical reactions and on shape of solids residue, we came to a conclusion concerning the mechanism of oxidation in autoclave. The results show that modelling of the process parameters of oxidation in autoclave can be used to predict efficiency of pre-treatment of sulphide refractory ores for valorisation of gold.*

Key words: polymetallic ore, gold, oxidation, oxygen, hydrometallurgy

INTRODUCTION

Today high-grade gold ores are almost entirely exploited, so that low grade ores and ores from which gold could not be easily extracted became the only source of precious metals (Maslenickii 1987, Zelikman 1983, Habaschi 1998, Maslenickii 1969, Sinadinovic 1998).

Gold could not be extracted from low-grade ores with satisfactory degree of extraction, therefore it is known as refractory gold. The term "refractory" applies to ores, which do not yield a sufficient gold and silver recovery if processed through conventional cyanidation. Sulphide ores where gold is encapsulated in a sulphide matrix

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as of submicron size particles [Maslenickii 1969, Sinadinovic 1998, Schweigart 1986, Jha 1987, Hausen 1989, Kontopoulos 1988, Vracar 2001) have turned out to be the hardest to process. Gold cannot be liberated by fine grinding, so that the efficiency of cyanide leaching process is low (Jha 1987, Hausen 1989, Kontopoulos 1988, Vracar 2001).

The main task of extractive metallurgy of gold is to find a suitable pre-treatment for refractory ores, which could provide high extraction of gold.

There are several pre-treatment procedures, which could be used to process the refractory gold ores. But from economic, metallurgical and ecological point of view the prospectus pre-treatment of refractory gold ores its pressure of oxidation in autoclaves (Kontopoulos 1988, Vracar 2001, Papangelakis 1990, Kontopoulos 1990, Mason 1985).

All processes, which involve hydrometallurgical treatment of raw materials are suitable for processing of not just oxides, but also sulphide ores and concentrates.

Table 1. The major reaction of oxidation of Fe, Cu and Zn sulphides and Gibbs energies at 298 and 473 K under pressure 101.325 kPa.

	Reaction	$-\Delta G^0$ (298 K)	$-\Delta G^0$ (473 K)
Fe 1	$\text{FeS}_{2(s)} + \text{H}_2\text{O}_{(l)} + 7/2 \text{O}_{2(g)} = \text{FeSO}_{4(aq)} + \text{H}_2\text{SO}_{4(aq)}$	1117.6	1019.6
Fe 2	$\text{FeS}_{2(s)} + 2 \text{O}_{2(g)} = \text{FeSO}_{4(aq)} + \text{S}_{(s)}^0$	664.77	611.44
Fe 3	$2 \text{S}_{(s)}^0 + 3 \text{O}_{2(g)} + 2 \text{H}_2\text{O}_{(l)} = 2 \text{H}_2\text{SO}_{4(aq)}$	905.66	816.42
Fe 4	$2 \text{FeSO}_{4(aq)} + \text{H}_2\text{SO}_{4(aq)} + 1/2 \text{O}_{2(g)} = \text{Fe}_2(\text{SO}_4)_3(aq) + \text{H}_2\text{O}_{(l)}$	160.19	137.83
Fe 5	$\text{FeS}_{(s)} + 2 \text{O}_{2(g)} = \text{FeSO}_{4(aq)}$	724.98	663.08
Fe 6	$\text{Fe}_2(\text{SO}_4)_3(aq) + 3 \text{H}_2\text{O}_{(l)} = \text{Fe}_2\text{O}_3(s) + 3 \text{H}_2\text{SO}_{4(aq)}$	-160.8	-152.10
Fe 7	$3\text{Fe}_2(\text{SO}_4)_3(aq) + 12 \text{H}_2\text{O}_{(l)} = 2\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \times 2\text{H}_2\text{O}_{(s)} + 5\text{H}_2\text{SO}_{4(aq)}$	1214.6	1302.1
Fe 8	$2 \text{FeSO}_{4(aq)} + 1/2 \text{O}_{2(g)} + 5 \text{H}_2\text{O}_{(l)} = 2 \text{Fe}(\text{OH})_3(s) + 2 \text{H}_2\text{SO}_{4(aq)}$	-44.69	-78.87
Fe 9	$\text{Fe}_2(\text{SO}_4)_3(aq) + n (\text{H}_2\text{O})_{(l)} = \text{Fe}_2\text{O}_3 \times (n-3) \text{H}_2\text{O}_{(s)} + 3 \text{H}_2\text{SO}_{4(aq)}, n=4$	-165.7	-164.29
Fe 10	$\text{FeS}_{2(s)} + \text{CuSO}_{4(aq)} = \text{CuS}_{(s)} + \text{FeSO}_{4(aq)} + \text{S}_{(s)}^0$	52.91	63.85
Cu 1	$\text{CuFeS}_{2(s)} + \text{H}_2\text{SO}_{4(aq)} + 1/4 \text{O}_{2(g)} + 1/2 \text{H}_2\text{O}_{(l)} = \text{CuSO}_{4(aq)} + \text{Fe}(\text{OH})_3(s) + 2\text{S}_{(s)}^0$	367.16	314.14
Cu 2	$\text{CuFeS}_{2(s)} + \text{H}_2\text{SO}_{4(aq)} + 1/2 \text{O}_{2(g)} = \text{CuS}_{(s)} + \text{FeSO}_{4(aq)} + \text{S}_{(s)}^0 + \text{H}_2\text{O}_{(l)}$	214.19	230.49
Cu 3	$\text{Cu}_5\text{FeS}_4(s) + 2 \text{H}_2\text{SO}_{4(aq)} + \text{O}_{2(g)} = 4 \text{CuS}_{(s)} + \text{CuSO}_{4(aq)} + \text{FeSO}_{4(aq)} + 2\text{H}_2\text{O}_{(l)}$	383.25	339.67
Cu 4	$\text{Cu}_5\text{FeS}_4(s) + \text{H}_2\text{SO}_{4(aq)} + 1/2 \text{O}_{2(g)} = \text{Cu}_2\text{S}_{(s)} + 3 \text{CuS}_{(s)} + \text{FeSO}_{4(aq)} + \text{H}_2\text{O}_{(l)}$	212.54	194.19
Cu 5	$\text{CuS}_{(s)} + \text{H}_2\text{SO}_{4(aq)} + 1/2 \text{O}_{2(g)} = \text{CuSO}_{4(aq)} + \text{H}_2\text{O}_{(l)} + \text{S}_{(s)}^0$	159.02	139.38
Cu 6	$\text{Cu}_2\text{S}_{(s)} + 5/2 \text{O}_{2(g)} + \text{H}_2\text{SO}_{4(aq)} = 2 \text{CuSO}_{4(aq)} + \text{H}_2\text{O}_{(l)}$	782.56	693.07
Cu 7	$\text{Cu}_2\text{S}_{(s)} + \text{O}_{2(g)} + 2 \text{H}_2\text{SO}_{4(aq)} = 2 \text{CuSO}_{4(aq)} + \text{S}_{(s)}^0 + 2\text{H}_2\text{O}_{(l)}$	329.73	284.86
Cu 8	$\text{Cu}_2\text{S}_{(s)} + 1/2 \text{O}_{2(g)} + \text{H}_2\text{SO}_{4(aq)} = \text{CuSO}_{4(aq)} + \text{CuS}_{(s)} + \text{H}_2\text{O}_{(l)}$	170.71	145.48
Cu 9	$\text{CuS}_{(s)} + 2\text{O}_{2(g)} = \text{CuSO}_{4(aq)}$	611.85	547.59
Cu 10	$\text{Cu}_2\text{S}_{(s)} + 2 \text{Fe}_2(\text{SO}_4)_3(aq) = 2 \text{CuSO}_{4(aq)} + 4 \text{FeSO}_{4(aq)} + \text{S}_{(s)}^0$	9.35	9.19
Zn 1	$\text{ZnS}_{(s)} + \text{H}_2\text{SO}_{4(aq)} = \text{ZnSO}_{4(aq)} + \text{H}_2\text{S}_{(g)}$	16.49	31.76
Zn 2	$\text{ZnS}_{(s)} + \text{H}_2\text{SO}_{4(aq)} + 1/2 \text{O}_{2(g)} = \text{ZnSO}_{4(aq)} + \text{S}_{(s)}^0 + \text{H}_2\text{O}_{(l)}$	220.27	202.20
Zn 3	$\text{ZnS}_{(s)} + 2 \text{O}_{2(g)} + \text{H}_{(aq)}^+ = \text{Zn}^{2+}_{(aq)} + \text{HSO}_4^-(aq)$	705.96	629.69
Zn 4	$\text{H}_2\text{S}_{(g)} + 1/2 \text{O}_{2(g)} = \text{S}_{(s)}^0 + \text{H}_2\text{O}_{(l)}$	203.78	170.44
Pb 1	$\text{PbS}_{(s)} + \text{H}_2\text{SO}_{4(aq)} + 1/2 \text{O}_{2(g)} = \text{PbSO}_{4(s)} + \text{S}_{(s)}^0 + \text{H}_2\text{O}_{(l)}$	263.67	246.43
Pb 2	$\text{PbS}_{(s)} + \text{H}_2\text{SO}_{4(aq)} = \text{PbSO}_{4(s)} + \text{H}_2\text{S}_{(g)}$	59.88	75.99

The major reactions of the oxidation of relevant sulphides, are shown in Table 1. (Maslenickii 1987, Zelikman 1983, Habaschi 1998, Maslenickii 1969, Vracar 2001, Vracar 1975, Vracar 1977, Vracar 1987, Vracar 1997, Long 1999) and Gibbs energies at 298 and 473 K. Gibbs energies were calculated using the HSC Chemistry software.

The values of $\Delta_r G^\circ$ indicate that there is a thermodynamic possibility of oxidation of the above sulphides into elementary sulphur and sulphates within temperature range 298–473K.

HYDROMETALLURGICAL OXIDATION OF SULPHIDE RAW MATERIALS IN AUTOCLAVES

Application of hydrometallurgical processes in extractive metallurgy dates from middle of last century. In the beginning these processes were used for extraction of Ni, Co and Cu from sulphide ores. From then there's been numerous investigations in this field.

Pioneer in using of autoclave technology in extractive metallurgy of sulphide ores is Canadian company Sherritt Inc. (Habaschi 1998, Maslenickii 1969), which started to use this technology for extraction of nickel. Since then this proces was developed to process of Zn concentrates and complex gold ores. Presently, the whole group of autoclave technologies is available in Canadian company Dynatec Corporation, Fort Saskatchewan, Alberta.

Raw materials used in our experiments are domestic sulphide concentrates:

- Pyrite concentrate, carrier of precious metals, which is product of flotation of polymineral raw materials (K1),
- FeS₂-Cu-Zn-Pb polymetallic collective flotation concentrate, with refractory precious metals (K2),
- Pb-Zn-Cu-FeS₂ polymetallic collective flotation concentrate (K3).

Different analytical and instrumental methods were used to characterize these concentrates: volumetric and gravimetric analysis, atomic adsorption spectroscopy (AAS), SEM and EDS analysis with quantitative analysis of size and shape of particles, RDA analysis, AES-ICP, differential thermal analysis (DTA), and thermo gravimetric analysis (DTA).

Analysis show that all three concentrates are mostly made of iron and sulphur. They also contain small amounts of copper, zinc, lead and arsenic. Contents of other elements are not significant. (Table 2). First two concentrates contain small amounts of gold and silver, while in concentrate K3 their content is considerable.

Table 2. Chemical analysis of input concentrates (% w/w)

	Fe	S	Cu	Zn	Pb	As	Au, g/t	Ag, g/t
K1	45.96	48.00	0.60	-	-	0.70	49.5	27.5
K2	19.46	30.55	6.50	6.375	1.8	0.91	24.2	182.7
K3	23.18	31.29	2.00	9.16	10.40	0.32	598.7	485.8

Granulometric analysis of concentrates gives Gauss type distribution curve with maximum at particle size of 20-30 μm and frequency of appearance of 60%.

From polished surfaces of concentrates samples one can see that basies of them is made of pyrite. In first two concentrates visible gold is not detected, therefore that one can conclude that gold is completely associated in pyrite, so that it's accessibility to common leaching solutions does not exist. In concentrate K2 gold and copper, zinc and lead minerals are captured in pyrite, therefore a secondary refractoriness appears. From all of above it comes that pre-treatment is necessary to extract precious metals from this kind of ores. On the other hand, in concentrate K3 visible gold particles (10-15 μm) are detected, so that the K3 concentrate has little refractoriness comparing to the first two concentrates and gold could be extracted from it with common leaching solutions without any pre-treatment.

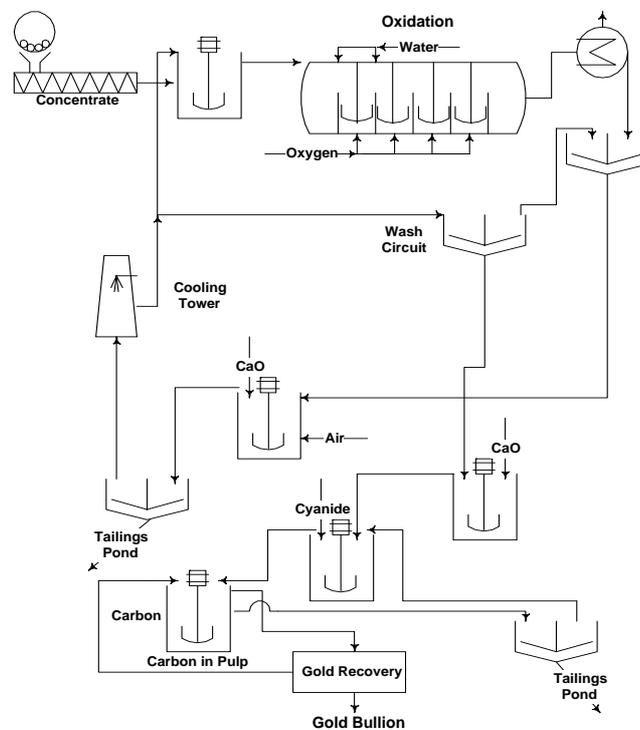


Fig. 1. Diagram of autoclave oxidation with operation stream

Process of autoclave oxidation is shown in Figure 1. with all process parameters. Pressure oxidation is conducted at 200°C at oxygen pressure of 2MPa, and with constant stirring with propeller mixer (200 rpm). Experimental research (Vracar 2001) has shown that the oxidation is predominantly influenced by temperature and time, so that high degree of transfer of most metals (except lead) into solutions can be achieved

by applying the partial oxygen pressure of 2 MPa, S/L ratio of 80 g/dm³ with technically and technologically justified particle size as well as adequate choice of temperature and time. The residue after the oxidation can be successfully processed by pyrometallurgical or hydrometallurgical methods in order to obtain precious metals. After completing of pressure oxidation the final solution contains Fe²⁺ and Fe³⁺ and copper and zinc (Cu²⁺, Zn²⁺). This solution can be used as a feed for extraction of copper and zinc, but valorisation of iron is not economically justifiable. Solid residue consist of iron, lead, gang materials and precious metals, as well.

Solid residues contains gold and gangue materials, lead transfers to solid as insoluble PbSO₄. Silver partially reacts making sulphates, goes into solid. Solid residue of autoclave oxidation contains precious metals and lead, which are released from pyrite matrix and become accessible to leaching solutions.

A microphotographs (figure 2.) of solid residues of concentrate K1 reveals irregularly shaped particles of several μm. There is also spekularite- iron oxide in sulphate basis. The needle shaped phase could be associated with gangue minerals, aluminosilicate contender of size of several μm. Spekularite is randomly disturbed throughout structure.



Fig. 2. SEM microphotographs solid residues of concentrate K1, a. spekularit in sulphide-iron basis, 10000×, b. spekularit with gangue minerals magnified 7500×

Solid residue of concentrate K2 is characterized with highly developed surface of sulphur compounds of iron and lead. Besides particles, gangue minerals (SiO₂) could be detected in this microphotographs (figure 3.). Sulphur compounds of barium and iron are in feather shaped particles ~μm. This shape of particles have tendency to agglomerate. Feather shaped particles can capture gold, so this shape is not suitable.

In solids residue of concentrate K3 particles are usually like so finely grained agglomerated crystals. There are noticeable needle shaped crystals of spekularit, same as in residue of concentrate K1.

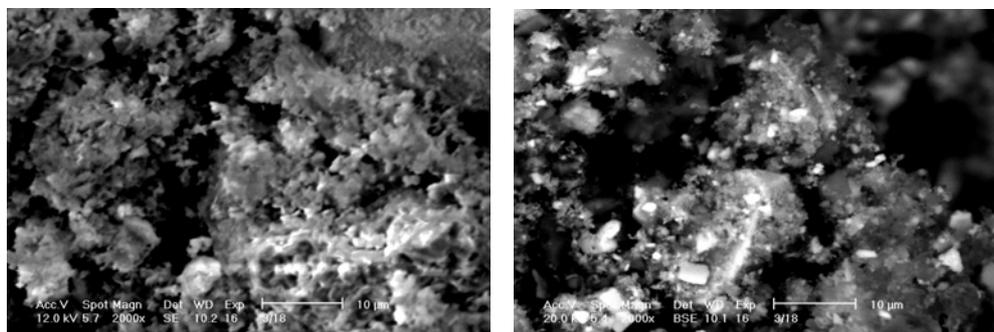


Fig. 3. SEM microphotographs solid residues of concentrate K2 III/18, a. magnified 200×, b. sulphur-salts with SiO₂, magnified 500×

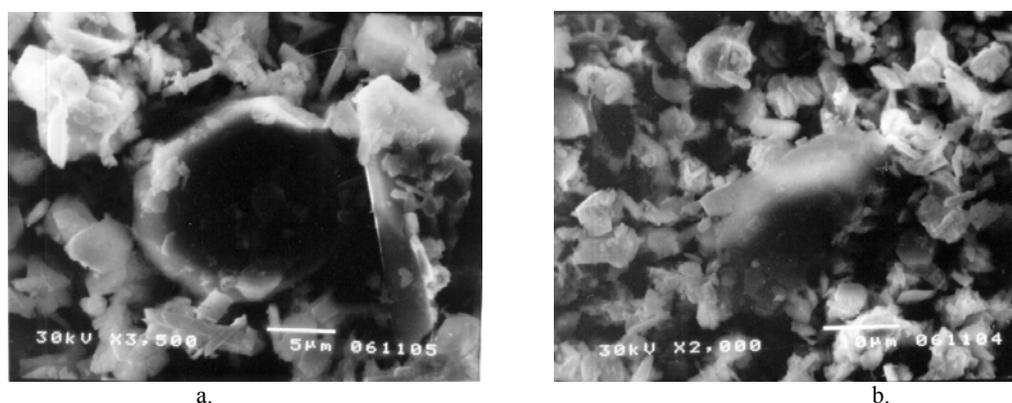


Fig. 4. SEM microphotographs solid residues of concentrate K3, a. sulphur-salts of iron and lead with SiO₂ in center, magnified 2000×, b. sulphur-salts of iron, magnified 3500×

Structural and morphological characteristic of solid residues for autoclave oxidation of studied concentrates are suitable for leaching with tiourea. All residues have a fine-grained structure. Effect is predominant of particle shape on the rate of solid-liquid separation velocity.

DISCUSSION

Pressure oxidation of sulphide ores and concentrates leads to new method of determination of level of refractoriness, and to applicability of this processes to different ores and economic feasibility of processes.

The dependence of recovery of refractory gold on oxidation of sulphide sulphur is shown at figure 5, (Berezowski 1991). This diagram represent dependences for some famous pyrite and arsenic-pyrite concentrates like as Porgera, Olympius, Campbell etc, together with concentrates used in this study K1, K2 and K3. For concentrates,

which have, even layout of gold in their structure the dependence is a straight line. This concentrates, like Porgera request high grade of oxidation of sulphide sulphur. On the other hand in Olympius concentrate gold is mostly associated in arsenic-pyrite, which can explain high rate of reaction and better reactivity.

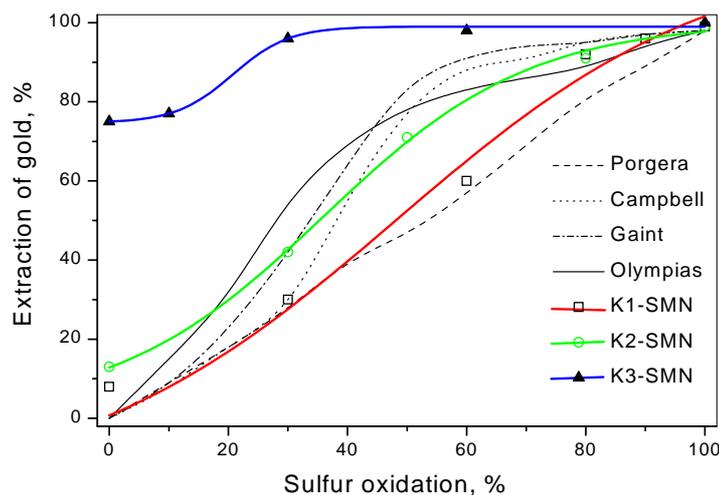


Figure 5. Extraction of gold in dependence of oxidation of sulphide sulphur

CONCLUSION

From characteristics of concentrates, processes, chemical reactions and structural-morphological changes of raw materials during pressure oxidation the mechanism of oxidation can be identified. Experimental results on chemical reactions and shape of solid grains remained after oxidation, modelling of the process parameters can be used to design efficient process of pre-treatment of sulphide refractory ores for valorisation of gold. By treating domestic polymetallic ores (gold is associated with sulphides of iron and copper), we can suggest the technology with great significant importance in both economic and ecological sense. Pressure oxidation and treatment of leaching by extraction of copper and zinc, as well as extraction of lead and precious metals from solid residue represents complex way of exploitation of useful components from concentrates and also reducing of global environment pollution.

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W pracy zostały przedstawione fizyczne i chemiczne zmiany jakim ulegają minerały siarczkowe żelaza, miedzi i cynku w trakcie ciśnieniowego utleniania. Utlenianie w autoklawie jest operacją przygotowawczą w przerobie trudnych do ługowania siarczkowych rud metali oraz koncentratów. Operacja ta jest konieczna dla „uwolnienia” złota, które zamknięte jest w matrycy z pirytu. Surowa ruda oraz półprodukty końcowe zostały scharakteryzowane. Na podstawie wyników reakcji chemicznych oraz kształtu otrzymanych produktów, można było wyciągnąć wnioski dotyczące mechanizmu procesu utleniania siarczków w autoklawie. Otrzymane wyniki pokazują, że modelowe parametry procesu utleniania w autoklawie, mogą zostać wykorzystane do przewidzenia korzyści uzyskiwanych z procesu przygotowania rud siarczkowych pod kątem ekstrakcji złota.