SELECTIVE AUTOCLAVE RECOVERY OF COPPER AND SILVER FROM WAELZ CLINKER IN AMMONIA MEDIUM

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ABSTRACT

Upon processing of zinc ferrite cakes in Waelz kilns a waste product, called Waelz clinker, is obtained. The copper and silver contents in this product are comparable to those of their ores which turns it into a valuable raw material.

In the present work the experimental results on selective autoclave leaching of Waelz clinker in ammonia medium are presented. The effect of main technological parameters on the degree of value metals recovery and iron precipitation is studied. It is established that the highest extend of copper and silver recovery is obtained under the following conditions: temperature 383 K, Po_2 0.4 MPa, ammonia concentration 110 g l^{-1}, ammonium sulfate concentration 70 g l^{-1}, pulp density 100 g $l^{-1}$and test duration 120 min. At these conditions 86,5 % of copper and 68,5 % of silver are solubilized, whereupon over 99 % of iron is hydrolytically precipitated. The composition of the corresponding leach solution is: 1,22 g l^{-1}Cu, 10 mg l^{-1} Ag, 90 mg l^{-1} Zn, 30 mg l^{-1} Fe and 40 mg l^{-1} Mn.

Keywords: autoclave leaching, Waelz clinker, copper, silver, ammonia medium.

INTRODUCTION

The currently applied method for processing of zinc-ferrite cakes at KCM AD is the so called Waelz rotary kiln process. This process consists of reduction and volatilization of the non-ferrous metals in a rotary kiln. The kiln has 2 - 3% inclination and rotates at about 1 rpm. The charge consists of zinc-ferrite cakes, coke breeze and binder (sand). The process has long history (more than 100 years) and established technology status (listed as Best Available Technology [1]).

The volatile metals (Zn, Pb, Cd) are reduced to their metallic state, sublime into the free atmosphere of the furnace and are finally reoxidized with an air current, obtaining impure oxides with high concentration of Zn and Pb, aside other impurities. These impure oxides are called Waelz oxides. This is the main product which is further processed for zinc, lead and cadmium recovery.

The other product of the process is the furnace slag called Waelz clinker which consists of the following main minerals - magnetite, hematite, troilite, jarosite, siderite, metallic iron, pyrite, bornite, chalcocite, arsenopyrite, pyrrhotite, galena, sphalerite (10 - 15 %), also oxides, sulphates and carbonates of calcium, iron, lead, zinc and copper (5 %), aluminosilicates of potassium, sodium, magnesium, iron, lead and copper (20 - 25 %) and carbon [2]. The elevated concentrations of copper (1 - 3 %), carbon (15 - 20 %) and silver (about 200 g t^{-1}) converts the Waelz clinker into a valuable raw material.

Many methods for Waelz clinker processing have been developed in recent years, but up to this moment an effective technology allowing complete recovery of the valuable metals is not available [3 - 7]. Currently the applied method for clinker processing at KCM AD is floatation which yields copper-silver concentrate and coke concentrate with unsatisfactory recovery of the value metals. Thus the task for development of Waelz clinker processing technology is still actual.

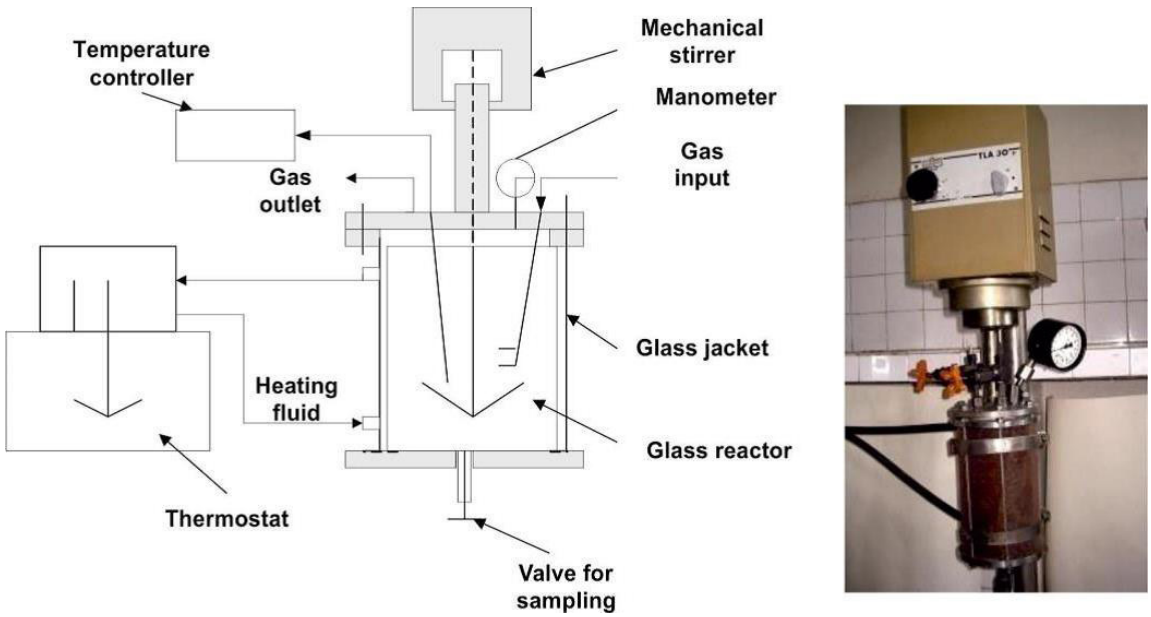

Fig. 1. Scheme of the laboratory equipment for autoclave leaching of Waelz clinker.

The aim of the present experimental work is to investigate the process of selective autoclave recovery of silver and copper from Waelz clinker waste in ammonia medium. The effect of the main technological parameters on the degree of value metals recovery and iron hydrolytic precipitation is also determined.

EXPERIMENTAL

Methodology of study

The laboratory experiments are conducted in glass autoclave model TLA 30 with 2 l capacity. The scheme of the laboratory equipment for autoclave leaching of Waelz clinker waste is shown on Fig. 1. The autoclave

Table 1. Chemical composition of the Waelz clinker, %.

Cu	Fe	Ag, g t^{-1}	C	Mn	Zn	Pb	As	Si	Al	Na	K	Ca	Mg	S
1,92	36,87	128	3,55	1,53	0,33	0,19	0,06	12,55	7,27	0,75	0,40	4,74	1,25	4,3

Table 2. Test conditions and chemical compositions of the leaching products upon autoclave dissolution of Waelz clinker with different complexing salts.

Test conditions				Leaching products	Chemical composition, %				
NH_3 g l^{-1}	Complexing salt	T, °C (P_{O2}, MPa)	Pulp density (τ , min)		Cu	Ag, g t^{-1}	Fe	Mn	Zn
12,5	25 g.l^{-1} $(NH_4)_2SO_4$	80 (0,4)	10 % (120)	Solution, g.l^{-1} Residue, %	1,30 0,94	- 134	0,03 28,4	Traces 1,68	0,17 0,29
12,5	25 g.l^{-1} $(NH_4)_2CO_3$	80 (0,4)	10 % (120)	Solution, g.l^{-1} Residue, %	1,20 0,81	- 125	0,014 24,0	0,005 1,76	0,05 0,29
12,5	25 g.l^{-1} NH_4Cl	80 (0,4)	10 % (150)	Solution, g.l^{-1} Residue, %	1,16 0,86	- 109	0,018 27,40	0,003 1,63	0,07 0,35
12,5	25 g.l^{-1} NH_4NO_3	80 (0,4)	10 % (120)	Solution, g.l^{-1} Residue, %	1,23 0,87	- 115	0,021 33,6	0,002 1,62	0,10 0,25

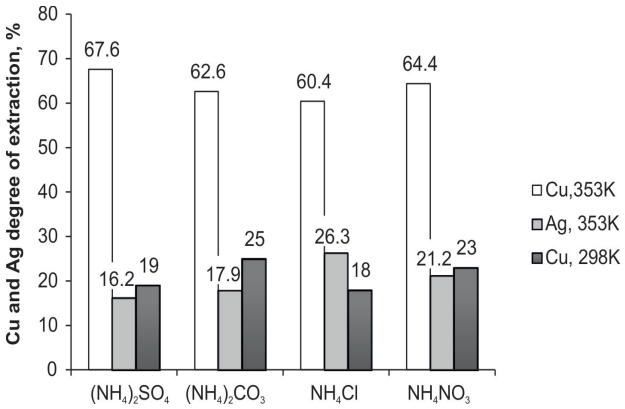

Fig. 2. Copper and silver degree of recovery upon autoclave dissolution of Waelz clinker with different complexing salts.

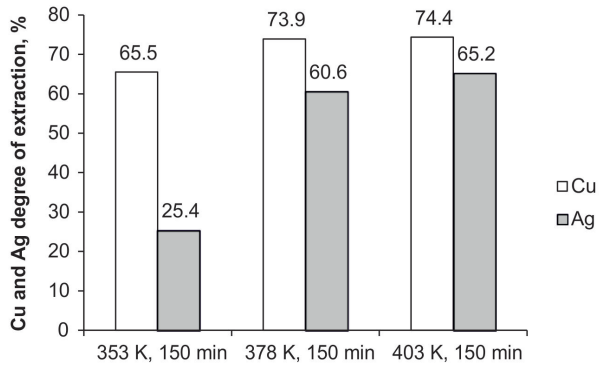

Fig. 3. Copper and silver degree of extraction upon autoclave dissolution of Waelz clinker at different temperatures.

allows reaching the maximum operating temperature of 423 K, pressure of 1.8 MPa, agitation 1000 min^{-1}. Reducer valve is mounted at the bottom of the autoclave, allowing sampling during the experiment. For determination of the degree of metals extraction from the Waelz clinker over a period of time, a sample was taken from the pulp for analysis of their concentration in the solution. After completion of the experiments the obtained pulp is filtered and the residue is desiccated at 353 K for 24 h and weighed on an assay balance. The concentrations of Cu, Ag, Fe, Mn and Zn in the production solutions and in the solid residue are determined by means of AAA (Perkin-Elmer 5000) and ICP-OES (Prodigy) analyses. The distribution of silver between the leaching products is determined on the basis of chemical analysis of the solid residue.

Chemical analysis of the Waelz clinker

The chemical composition of the Waeltz clinker determined by means of AAA and ICP-OES analyses is given in Table 1. As can be seen from Table 1 the copper and silver content in Waelz clinker is a relatively high - comparable to those of copper ores. Furthermore, the clinker is characterized by a high iron, silicon, carbon and aluminum content which will affect the value metals behavior upon autoclave leaching.

RESULTS AND DISCUSSION

Effect of the type of complexing salt

Initially experiments with different complexing salts (NH_4Cl, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$ and NH_4NO_3) at constant other parameters are carried out. The conditions of the conducted experiments and the composition of the leaching product are presented in Table 2. The obtained degree of copper and silver extraction is presented on Fig. 2. For comparison on the same figure are given the degrees of copper and silver recovery at ambient temperature and oxygen pressure.

It can be seen from the figure that the copper degree of extraction does not varies significantly upon autoclave leaching of the clinker in the presence of different complexing salts (from 60,4 to 67,6 %). The extraction degree of silver is more dependent on the type of the complexing salt and varies between 16,2 and 26,3 %. The degree of copper extraction upon autoclave leaching is considerably higher than at ambient conditions, vice versa the leachability of silver is poorer at autoclave conditions in the presence of ammonium sulfate and ammonium carbonate.

The chemical compositions of the obtained leach solutions are very similar and also the concentrations of the minor impurities varies in very short limits, g l^{-1}: 1,15 - 1,23 Cu 0,014 - 0,03 Fe, 0,002 - 0,003 Mn, 0,07 - 0,10 Zn.

It is established that over 99 % of the iron and manganese are precipitated, where the carbon and the gangue minerals presented in the clinker also concentrates.

Based on the preliminary experiments the ammonium sulfate is chosen as a complexing salt and the rest of the tests are conducted in the $NH_3 - (NH_4)_2SO_4$ system.

Effect of the temperature

For the assessment of the influence of this parameter series of experiments with duration of 120 min

Table 3. Test conditions and chemical compositions of the leaching products upon autoclave dissolution of Waelz clinker at different temperatures.

Test conditions		Leaching products	Chemical composition, %				
T, K (P_{O2}, MPa)	Pulp density (τ ,min)		Cu	Ag, g t^{-1}	Fe	Mn	Zn
353 (0,4)	10 % (150)	Solution, g l^{-1} Residue, %	1,26 0,76	- 112	0,01 21,3	0,002 1,79	0,09 0,24
353 (0,4)	10 % (120)	Solution, g l^{-1} Residue, %	1,20 0,96	- 134	0,03 28,4	Traces 1,68	0,17 0,29
378 (0,4)	10 % (150)	Solution, g l^{-1} Residue, %	1,42 0,72	- 74	0,01 20,8	Traces 1,84	0,01 0,28
403 (0,4)	10 % (150)	Solution, g l^{-1} Residue, %	1,43 0,70	- 63	0,01 21,3	Traces 1,81	0,01 0,26

are conducted. The experiments are carried out in the NH_3 - $(NH_4)_2SO_4$ system at initial concentrations of NH_3 12,5 g l^{-1} and $(NH_4)_2SO_4$ 25 g l^{-1}. The test conditions and the chemical compositions of the leach solutions and residues are systematized in Table 3. The final degrees of copper and silver extractions into solution are presented on Fig. 3.

It is seen from the results that with the increase of temperature from 353 to 403 K the copper and silver extraction degree increases significantly, whereupon the increment is stronger for silver (from 16,2 to 65,2 %). It is also observed decrease of Fe and Mn concentrations in the solution with the increase of temperature (down to 10 mg l^{-1} Fe and traces of Mn).

The increase of dissolution time from 120 to 150 min (temperature 353 K) has minor effect on copper and silver recovery degree.

It can be assumed that the incomplete metals recovery in solution is due to the high carbon concentration in the Waelz clinker (about 13 %), that acts as a sorbent of copper and silver ions. This fact is proven by our previous research results [8, 9]. For enhancement the desorption process and rising the metals extraction degree, the ammonia concentration should be increased.

Effect of the reagent concentrations and oxygen partial pressure

A series of experiments with different initial concentrations of ammonia and ammonium sulfate is carried out to check out the assumption that sorption of coper and silver takes place upon autoclave leaching of Waelz clinker. The test conditions and the compositions of the production solutions and solid residues are pointed

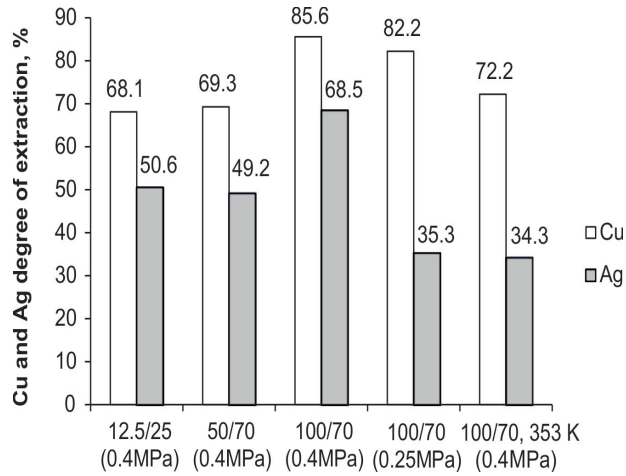

Fig. 4. Copper and silver degree of extraction upon autoclave dissolution of Waelz clinker at various reagent concentrations and oxygen partial pressure.

Table 4. Test conditions and chemical compositions of the leaching products upon autoclave dissolution of Waelz clinker at various reagent concentrations and oxygen partial pressure.

Test conditions			Leaching products	Chemical composition, %				
τ, min	NH_3, g l^{-1} $(NH_4)_2SO_4$, g l^{-1}	T, K P_{O2}, MPa		Cu	Ag, g t^{-1}	Fe	Mn	Zn
150	12,5 (25)	378 (0,4)	Solution, g l^{-1} Residue, %	1,31 0,72	- 76	0,01 20,8	Traces 1,84	0,01 0,28
150	50 (70)	378 (0,4)	Solution, g l^{-1} Residue, %	1,33 0,68	- 79	0,02 21,0	0,02 1,65	0,11 0,26
150	100 (70)	378 (0,4)	Solution, g l^{-1} Residue, %	1,64 0,35	- 60	Traces 22,7	Traces 1,62	0,14 0,17
150	100 (70)	378 (0,25)	Solution, g l^{-1} Residue, %	1,58 0,39	- 104	0,03 19,4	0,04 3,10	0,09 0,58
150	100 (70)	353 (0,4)	Solution, g l^{-1} Residue, %	1,39 0,59	- 107	0,04 18,6	0,08 2,23	0,10 0,23

Table 5. Test conditions and chemical compositions of the leaching products upon autoclave dissolution of Waelz clinker at different pulp density.

Test conditions			Leaching products	Chemical composition, %				
τ, Min	Pulp density	T, K (P_{O2}, MPa)		Cu	Ag, g t^{-1}	Fe	Mn	Zn
150	5 %	378 (0,4)	Solution, g.l^{-1} Residue, %	0,65 0,78	- 71	0,01 30,3	0,007 1,54	0,08 0,21
150	10 %	378 (0,4)	Solution, g.l^{-1} Residue, %	1,33 0,68	- 79	0,02 21,0	0,02 1,65	0,11 0,26
150	20 %	378 (0,4)	Solution, g.l^{-1} Residue, %	2,46 0,97	- 106	0,04 22,4	0,05 1,60	0,25 0,21

in Table 4. The resulting degree of copper and silver recovery is plotted on Fig. 4.

It is clear from the obtained results that the increase of the initial reactants concentration has a positive effect on copper and silver extent of recovery. At all tests quantitative iron and manganese precipitation is observed.

The oxygen partial pressure is parameter having effect on the rate of chemical dissolution of the metal compounds and on the degree of iron oxidation and its hydrolysis. It is observed that the rise of oxygen partial pressure from 0.25 to 0.4 MPa did not affect copper degree of recovery, but led to significant increment of silver dissolution (over 30 %).

Effect of pulp density

The effect of this parameter on the value metals degree of recovery is assessed at temperature 378 K, initial concentrations of NH_3 50 g l^{-1} and $(NH_4)_2SO_4$ 70 g l^{-1}, pulp density 5, 10 and 20 %. The test conditions and obtained experimental results are presented in Table 5.

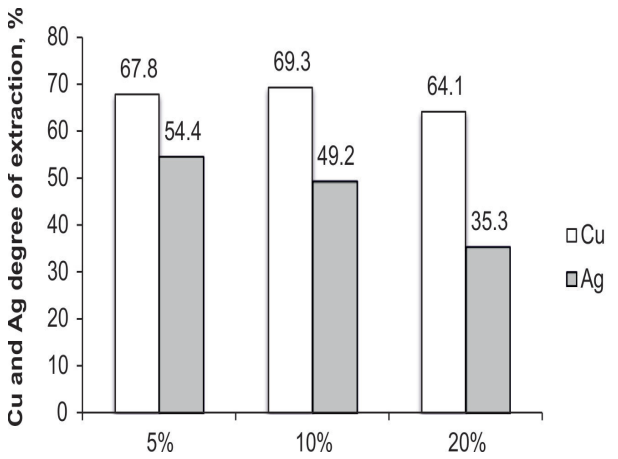

Fig. 5. Copper and silver degree of extraction upon autoclave dissolution of Waelz clinker at various pulp densities.

The calculated degrees of copper and silver recovery are given in Fig. 5.

It can be deduced from the experimental results that the decrease of pulp density from 10 to 5 % (respectively increase in the aqueous phase volume) led to slight rise of the value metals recovery degree but also resulted in declination of their concentration into the leach solution (below 1 g l^{-1} Cu), which reduces the process productivity and enlarges the equipment volume. It is favorable from a practical point of view the process to be conducted at pulp density 10 %.

CONCLUSIONS

The effect of the main technology parameters on copper and silver recovery upon selective autoclave ammonia leaching of the Waelz clinker is determined. It is established that they have stronger effect on silver leachability than on copper. Maximal degree of value metals dissolution is obtained at temperature of 378 K, oxygen partial pressure of 0.4 MPa, ammonia concentration of 100 g l^{-1} and pulp density of 10 % for 120 min. At these conditions 85,6 % of Cu and 68,5 % of Ag are extracted in the ammonia solution, whereupon over 99 % of iron and manganese are precipitated in the residue. The production solution contains 1,22 g l^{-1} Cu, 10 mg l^{-1} Ag, 90 mg l^{-1} Zn, 30 mg l^{-1} Fe and 40 mg l^{-1} Mn. The incomplete copper and silver recovery is due to the higher carbon (coke) content in the Waelz clinker which acts as a sorbent of the value metals. For quantitative copper and silver recovery the process has to be carried out in two stages: carbon removal stage and leaching stage.

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