



METHOD FOR ALUMINUM DROSS UTILIZATION

Assis.Prof.B.Lucheva, Assoc.Prof.Dr. R.Petkov and Assis.Prof.Tz.Tzonev

University of Chemical Technology and Metallurgy, 8 Kl. Ohridsky Blvd., Sofia, Bulgaria

Abstract: A new hydrometallurgical method has been developed for metal aluminum utilization from secondary aluminum dross. Secondary aluminum dross is a powder product with an average of 35% aluminum content (below 1mm). It is waste from primary aluminum dross pyrometallurgical fluxless treatment in rotary DC electric arc furnace.

This method is based on aluminum leaching in copper chloride water solution. As a result an aluminum oxychloride solution and solids, consisting of copper and oxides are obtained. In order to copper chloride solution regenerate hydrochloric acid is added to the solids. The process is simple, quick, economic and safe.

The aluminum oxychloride solution contains 56 g/l Al_2O_3 . The molar ratios are $Al:Cl=0,5$; $OH:Al=1$. The solution has 32% basicity and 1,1 g/cm³ density. For increasing the molar ratio of aluminum to chlorine aluminum hydroxide is added to this solution at 80°C. Aluminum hydroxide is the final product from the secondary aluminum dross alkaline leaching

As a result aluminum oxychloride solution of the following composition is prepared: Al_2O_3 – 180 g/l; $Al:Cl=1,88$; $OH:Al=4,64$; basicity 82%; density 1,22 g/cm³, pH=4-4,5.

Aluminum oxychloride solution produced by means of this method can be used in potable and wastewater treatment, paper making, in refractory mixture as a binder etc.

INTRODUCTION

The object of this study is secondary aluminum dross, which result from a primary aluminum dross pyrometallurgical fluxless processing in a rotary DC electric arc furnace [1]. It is a powder product with an average of 35 % metal content and of chemical composition as shown in Table 1.

Table 1: Metal chemical composition, %

Mg	Al	Si	Mn	Fe	Cu	Zn
0,00	90,28	5,93	0,34	1,10	1,82	0,53

Table 2 provides the element composition of secondary aluminum dross, which is analyzed by AES ICP following alkaline melting and leaching as well as by the classical chemical methods.

Table 2: Element composition of secondary aluminum dross, %

Al	Mg	Si	Mn	Fe	Cu	Zn	Ti	Ca	Na	S	P	K
63,57	3,83	2,68	0,11	1,22	0,63	0,18	0,31	0,79	0,12	0,26	0,01	0,13

Aluminum is found in the dross mainly as metal aluminum – 31,5%, aluminum nitride – 9,5% and aluminum oxide – 49%. In addition, the dross contains minor amounts of oxides and other components of Ti, Cu, Fe, Ca, Zn, S, K and Na.

The metal content in the dross depending on the granulometric composition varies as follows:

- 1mm+0,63mm 49,65%;
- 0,63mm+0,25mm 47,55%;
- 0,25 mm 25,00%;
- 0,1 mm 13,56%.

Secondary aluminum dross is valuable and less expensive raw material because of its high metal



content and it can effectively be utilized for different aluminum salt production.

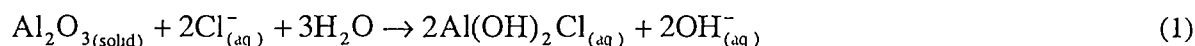
The purpose of this study is to investigate the possibility for secondary aluminum dross utilization for aluminum oxychloride production, which has several industrial applications – in the cosmetics industry as an active ingredient, as tanning agents and as flocculants for water treatment, in the preparation of refractory substances and inorganic fibers.

EXPERIMENTAL

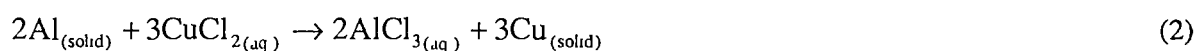
Aluminum oxychloride has traditionally been obtained by chemical processes such as double conversion of other basic aluminum salts, by partial hydrolyses of anhydrous aluminum chloride, by thermal split-off of hydrogen chloride from aluminum chloride-hexahydrate or by reaction of aluminum hydroxides. Aluminum oxychloride has also been prepared by electrochemical processes, which require the use of a specially prepared electrolysis cell, involving high-energy costs. On the other hand, special precaution must be taken regarding protection of the environment [2,3].

The purpose of the present research work is to investigate the aluminum recovery from secondary aluminum dross by copper chloride solution.

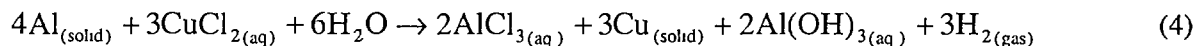
On the aluminum surface there is always a protective layer of aluminum oxide. In the copper chloride solution chloride ions destroy the oxidic surface layer of aluminum after:



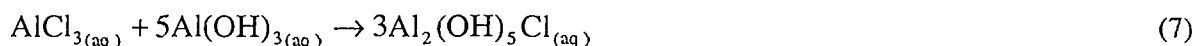
The reaction between metal aluminum free of the oxidic layer and copper chloride solution is a very complex one. The most probable reactions that take place are:



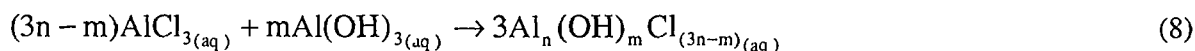
Thus the overall reaction can be written as follows:



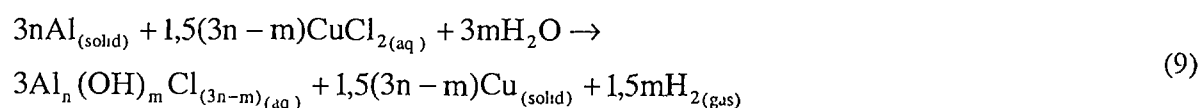
The reaction between AlCl_3 and $\text{Al}(\text{OH})_3$ can be expressed as follows:



or the most generally:



The total reaction can be described if the equation (2) is multiplied by $\frac{3n - m}{2}$, and equation (3) – by $\frac{m}{2}$ and sum up them.



The reaction (9) takes place in two steps: cementation and electrochemical dissolving of aluminum.



The cementation (equation 2) is a process of replacement of Cu(II) ions from the solution by less noble aluminum. The electric potential relations of Cu (II) and aluminum ions determine the thermodynamic possibility for this process. The standard electric potential of less noble aluminum is $-1,66\text{V}$ in comparison to the nobler copper $+0,34\text{V}$. The cementation process goes on until the two electric potentials become the same.

The following reaction may run off:



in small measure



in addition



During the second step of the process, the less noble aluminum is in metallic contact with the more noble copper in an aqueous aluminum oxychloride solution. In this way, a galvanic couple is formed. Aluminum is dissolved by galvanic action and goes into the solution and at the same time hydrogen is deposited at the nobler element.

The started copper chloride solution is 1M. Five samples of 20 ml are taken from this solution and then aluminum is added to them. The reacted quantity of aluminum is investigated as a function of time. The results are represented in Figure 1. The first step of the process is exothermic. The lack of blue colour when ammonia is added to the solution indicates that the copper concentration is low (below 100 ppm) and aluminum is effective in removing the copper from the solution.

As seen from Figure 1 only 90 min are sufficient for copper reduction. After that aluminum is dissolved electrochemically by means of galvanic element. The second step of the process carries out very slowly at room temperature and atmospheric pressure, which from practical point view is unacceptable.

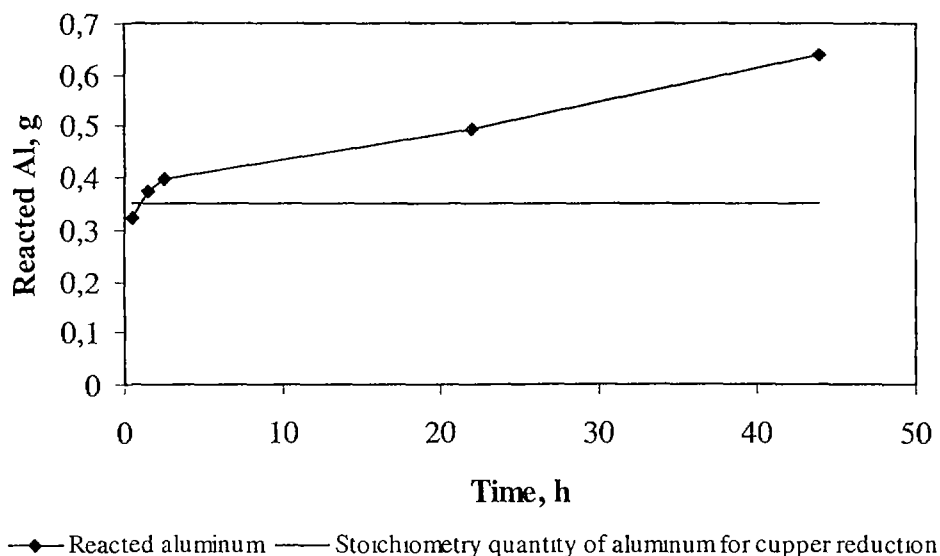


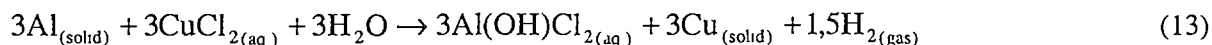
Figure 1: Reaction between metal aluminum and 1 M copper chloride solution

The choice of conditions for aluminum dissolving in copper chloride solution is determined by the desired type of aluminum oxychloride and by the desired aluminum concentration in the solution. For

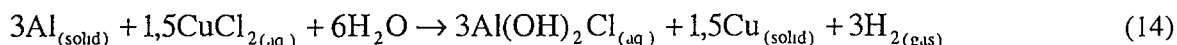


this purpose the following particular cases of reaction (9) are considered:

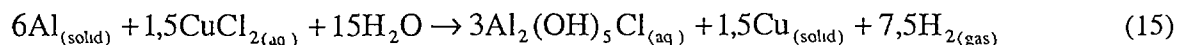
- n=1 and m=1



- n=1 and m=2



- n=2 and m=5



The conditions of the reactions for aluminum oxychloride prepared with a defined aluminum concentration are shown in Table 3.

Table 3: Different conditions of preparing aluminum oxychloride

Oxychloride	Aluminum g/l	Aluminum dross (25% metal aluminum) g	CuCl ₂ g/l	Reduced copper, g	Dissolved Al during first step, g	Dissolved Al during second step, g	Pulp density, g/l	H ₂ , l
Al(OH)Cl ₂	100	400	497,93	235,33	66,66	33,34	535,33	20,74
	75	300	373,44	176,50	49,99	25,01	401,50	15,56
	50	200	248,96	117,67	33,33	16,67	267,67	10,37
	25	100	124,48	58,83	16,66	8,34	133,83	5,19
Al(OH) ₂ Cl	100	400	248,96	117,67	33,33	66,67	417,67	82,96
	75	300	186,72	88,25	25,00	50,00	313,25	62,22
	50	200	124,48	58,83	16,66	33,34	208,83	41,48
	25	100	62,24	29,42	8,33	16,67	104,42	20,74
Al ₂ (OH) ₅ Cl	100	400	124,48	58,83	16,66	83,34	358,83	103,70
	75	300	93,36	44,13	12,50	62,50	269,13	77,78
	50	200	62,24	29,42	8,33	41,67	179,42	51,85
	25	100	31,12	14,71	4,17	20,83	89,71	25,93

The reactions (10)-(12) run off intensively at normal conditions up to a moment when the first step is completed. As shown in Table 1 the degree of metal aluminum recovery during the first step is the highest when the final product is Al(OH)Cl₂ - 66,66 %, while at Al₂(OH)₅Cl it is only 16,66%.

The least amount of hydrogen is produced in reaction (10) - only 0,5 g-mol, while according to reaction (12), from 1 g-mol dissolved Al, the hydrogen is 2,5 times more.

The quantity of cemented copper and insoluble oxides from aluminum dross determines the pulp density (Table 1). The least amount of copper is reduced after a reaction (12) in comparison with reaction (10) in which the cemented copper is 4 times more.

Thus, the reaction leading to formation of Al(OH)Cl₂ of 25 g/l aluminum concentration in solution can run safe and within short time. However, a disadvantage of this solution is low aluminum concentration.

Three fractions - 1+0,63; 0,63+0,25; -0,25 mm are dissolved in 1M copper chloride solution. The process is violent, because of the exothermic character of the cementation and aluminum nitride hydrolysis. In order to prevent strong gasing, the reaction vessel is cooled with water maintaining the process temperature at about 60° C. The process goes on for two hours. At these conditions aluminum



nitride practically is not hydrolysed [4]. Thus it prevents the release of ammonia. The pulp is left to stay overnight and then it is filtered to remove the remaining solids. The results are presented in Table 2.

The solid phase is calcinated at 200-300°C to transform cemented copper to a copper (II) oxide, which dissolves easier in hydrochloric acid. The started solution is regenerated by hydrochloric acid adding to calcined solid phase.

Aluminum from aluminum dross is in 50% excess according to the stoichiometry quantity (as shown in Table 2) for the copper reduction. The aluminum concentration in the resulting solution is determined (by complexometric titration), as well as the concentration of chlorine (by titrimetric method). The recovery degree of aluminum in solution is lowest at finest fraction –0,25 mm., probably due to the fact that the cathode aluminum surfaces are covered with separated copper, which makes difficult aluminum dissolving. In order to ensure free aluminum surface the process should be accompanied by stirring. However, with such stirring fine particles are formed and they stay in the solution after filtration.

As a result of experiments three solutions are obtained with almost equal aluminum concentration. The solution properties are shown in Table 4.

Table 4: Properties of aluminum oxychloride solution, produced by dissolving aluminum dross in copper chloride

Fraction	Al, g/l	Al ₂ O ₃ , g/l	Cl, g/l	Al:Cl	Al:OH	Density, g/cm ³	Basicity, %	pH
-0,25 mm	29,31	55,37	74,47	0,49	1,04	1,0967	32,00	3,9
-0,63+0,25 mm	29,65	56,00	76,24	0,51	0,96	1,0976	34,67	3,9
-1+0,63 mm	27,71	52,34	74,47	0,52	0,93	1,0965	35,67	3,9

These solutions are collected into one solution of 28,71 g/l aluminum concentration and 75,24 g/l chlorine concentration. The resulting aluminum chloride can be described as Al(OH)Cl₂. This solution has no practical use because of the low aluminum concentration, respectively molar ratio Al:Cl n Al:OH.

For increasing molar ratio Al:Cl greater than 0,5 experiments have been carried out. For this purpose, three samples of 100 ml have been used and different quantity of aluminum hydroxide added at temperature 80°C. Alkaline leaching of secondary aluminum dross forms this aluminum hydroxide. As a result three types of aluminum oxychloride solution are prepared (Table 5).

Table 5: Properties of aluminum oxychloride solutions

Solution	Al(OH) ₃ , g	Al, g/l	Al ₂ O ₃ , g/l	Cl, g/l	Al:Cl	OH:Al	Density, g/cm ³	Basicity	pH
started		28,71	54,23	75,24	0,50	1,00	1,1	34	3,9
1	8	55,90	105,60	72,69	1,01	2,01	1,12	66,98	4,0
2	15	80,00	151,12	72,73	1,44	2,31	1,19	76,92	4,0
3	22	100,50	189,83	73,3	1,88	4,64	1,22	82,26	4,2

Aluminum oxychloride solutions as per the experiment (Table 5) can be described as follows:

- solution 1 Al(OH)Cl₂
- solution 2 Al(OH)₂Cl
- solution 3 Al₂(OH)₅Cl.

AES ICP analyzes solution 2 from Table 4 for determining impurity concentration. The results are shown in Table 6.

Table 6: Impurity concentration of aluminum oxychloride, mg/l



Pb	Zn	Cu	Ni	Co	Cd	Na	K	Mg	Ca
<50	191	112	<10	10	<10	768	<200	1157	1575

The process for increasing molar ratio Al:Cl is simple and quick, up to 10-12% aluminum concentration in solution. In other conditions – higher temperature and higher pressure it may be possible to achieve ratios greater than two.

Aluminum oxychloride solution produced according this method can be effectively used in potable and wastewater treatment. For this purpose $Al_2(OH)_5Cl$ (solution 3) is investigated as a coagulant for raw water treatment. The experimented dose of the coagulant produced using the proposed method is 2,23 mg Al/. The results are presented in Table 7.

Table 7: Performance of aluminum oxychloride $Al_2(OH)_5Cl$ as a coagulant at temperature 19,8°C

	Water turbidity, mg/l	pH	Water color Pt-Co Scale	Total hardness of water mg-eq /l	Ca, mg/l	Mg, mg/l
Before treatment	14,1	7,1	20			
After treatment	0,8	7,0	<5	0,70	7	4,256

CONCLUSIONS

1. New hydrometallurgical method has been developed for utilization of metal aluminum from secondary aluminum dross. This method is based on aluminum leaching in copper chloride water solution. The process is simple, quick, economical and safe.
2. Resulting solution of aluminium oxychloride $Al(OH)Cl_2$ can be treated with aluminum hydroxide for increasing aluminum concentration in solution, depending on the desired final product.
3. Aluminum oxychloride $Al_2(OH)_5Cl$ produced according to this method can be effectively used as a coagulant in water treatment.

References:

- [1] Tzonev Tz.P., Mihovsky M.K., Lucheva B.I., Vasilev I.G., Pilot Rotary-Shaking Plasma Transferred Arc Furnace, 1st International Conference of the Chemical Societies of the South-East European Countries on Chemical Sciences and Industry, Halkidiki, Greece, June 1-4, (1998).
- [2] Solodova Lyudmila I., Galkin Yuriy M.; Bekenov Kajrat D., Shtern Emiliya K., Method Of Producing Aluminum Oxychloride Base Materials, SU1790549, (1993).
- [3] Bergner Dieter, Danner Max, Process For Preparing Basic Aluminum Chlorides, US4203812, (1980).
- [4] Fukumoto S., Hookabe T., Tsubakino H., Hydrolysis behavior of aluminum nitride in various solution, Journal of materials science 35, pp.2743-2748, (2000).