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SOME RESULTS OF RESEARCHES TO DEVELOP THE PROPER RECYCLING METHODS OF TECHNOLOGICAL RESIDUES FROM SECONDARY ALUMINUM INDUSTRY

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ABSTRACT

The objective of the research is to identify new suitable process to use residual waste (like aluminium secondary dross, salt slag or fly ashes) in concrete products according with sustainable industry concepts. The paper presents some results and directions of researches of recycling secondary aluminum industry by-products in Romania.

KEYWORDS: secondary aluminium dross, moulding mixture, casting, aluminium sulphate

1. Introduction

Aluminium technological residues named; dross, salts slag, black dross or salt cakes, are hazardous waste because it contains contaminants like soluble salts, oxides, carbides and sulphides as well as metallic aluminium which is entrapped in the slag. In contact with water it emits flammable gases such as acetylene or it is liable to give off toxic gases, such as ammonia, in dangerous quantities. Traditionally, aluminium wastes are disposed in landfill, costing the world aluminium industry an estimated $70 million. Resolutions of European Community regulation and spiralling costs are forcing the industry to consider alternatives. [2]. Worldwide Secondary Aluminium Industry produces nearly five million tonnes of furnace waste each year. Residual waste material is produced from any process in which aluminium is melted. For all that reasons a consortium of 7 partners decided to study the possibilities to process of technological residues from secondary aluminum industry and develop the proper methods to cut the production cost and to minimize or eliminate their disposed of in landfill. In the project there are involved three universities, two researches institutes and two aluminium companies. Transilvania Universiy Braşov, the manager of the project; National R&D Institute For Nonferrous And Rare Metals - IMNR, Technical University Of Civil Building Bucharest, Politehnica University – CCEEM Bucharest, INCDPM–ICIM Bucharest, partners, SC ALMET SA Năvodari, SC SILNEF SA, co-financing partners.

Romania has developed researches to find new methods to reduce landfilling of furnace waste and recover saleable products by soluble salts removal, use secondary aluminum technological waste for moulding mixture in foundry for iron heavy casting, obtain products which can be utilized like coagulants. Directions researches for process industrial secondary aluminium by products are showed in figure 1.

2. Experimental researches and results

The first researches were on the influence of technological process on mineralogical matrix of technological wastes from three secondary aluminium processors and their difference in function of their process conditions. As much as ranges of secondary aluminium technological wastes are large, the larger, there are metallic compounds spectrums, which are in the dross and ashes. As much as mineralogical compositions is complex the more difficult there is to process them for obtain useful products.

Complex mineralogical compositions need supplementary operations to separate, to soluble or to purify the useful compounds and for that there have to spend supplementary cost to process them.

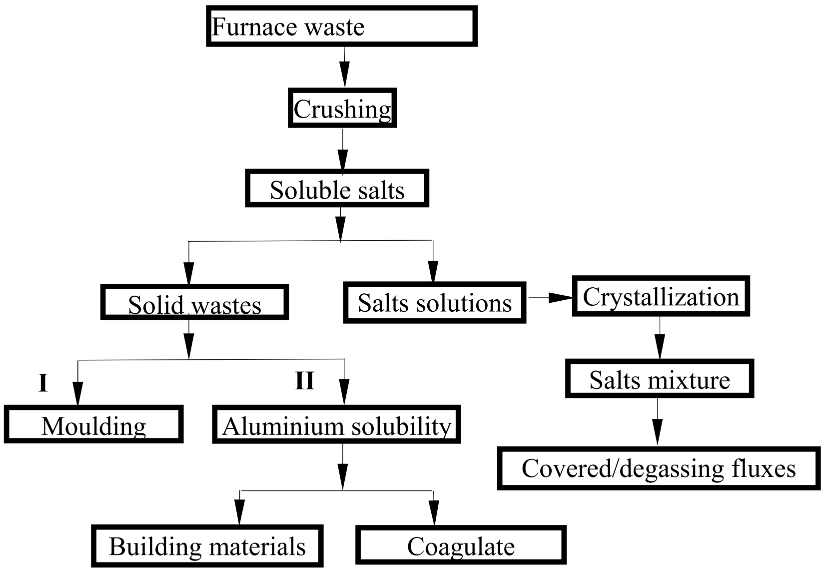

***Fig. 1.** Directions researches for process industrial secondary aluminium by products*

To study influence of technological process on mineralogical matrix of residues of the secondary aluminum industry there were take samples, from three different secondary aluminum companies:

The first company is SC ALMET SA Năvodari, which process scrap and spills to obtain casting alloys and wrought alloys for extrusion. For scrap melting they use revolving cylindrical furnace or crucible melting furnace. They work in quality system in conformity with SR EN ISO 9001:2001, SR EN ISO 14001:2005 and OHSAS 18001:2004 standards. To increase performance rating they use scrap sorting, melting deoxidizing, refining and filtering operations. The skimming from the first melt is in part reuse in their foundry circle. Technological residues are kept on the authorize slag dump till they are delivery to aluminum dross specialize processors. The second company is SC FABRIMIXT SA Câmpina, which process scrap, spills and dross to obtain ingot casting alloys. Technological residues are kept on their the authorize slag dump. For scrap melting they use revolving cylindrical furnace or crucible melting furnace. To increase performance rating they use melting deoxidizing, refining and filtering operations. The skimming from the first melt is in part reuse in their foundry circle. The third company is SC GEORGE IMPEX SRL Potcoava which process only aluminum dross from primary and secondary aluminum companies. For dross melting they use revolving cylindrical furnace or crucible melting furnace. The dross is crushed and the metal particles are sort from nonmetals components by shaking sieve. In the coarse faze there is more aluminum metallic thereby this part is melt to recover aluminum. The fine faze is technological residues and they are kept on the authorize slag dump. Then, those three secondary aluminum processors use the same furnace for melting but thy use the different starting material and they use different technological methods. One of the first analyses of process metallurgical methods influence can be observed from preliminary solid material balance for each company, table 1.

Table 1.

MATERIAL	Company					
	FABRIMIXT		ALMET		GEORGE IMPEX	
	t/ month	%	t/ month	%	t/ month	%
Aluminum scraps	160	73	250	71		0
Raw materials	10	5	30	9	10	10
Purchase dross	30	14		0	90	90
Dross from their foundry circle	20	9	70	20		0
Total	220	100	350	100	100	100
Casting alloys and wrought alloys	160	76	280	82	40	43
Technological residues	50	24	63	18	53	57
Loss	10	5	7	2	7	8
Total	210	100	343	100	93	100

These results show that technological residues percent depends on quality of started materials, which are processed. If for SC ALMET SA company the residues percent is ~18 % and ~ 24% for SC FABRIMIXT SA Câmpina company, for company SC GEORGE IMPEX SRL this percentage is more high ~57%. The samples were characterization by chemical analysis, particle size distribution analysis and phase analysis.

Chemical analysis were performed conform specific metallurgical nonferrous Romanian standards on each particle size distribution. The results show that the elemental compositions are distinct for each company. The results of our study show that the most important quantity of metallic aluminium there are in FABRIMIXT residues, which is follow by GEORGE IMPEX. Technological residues of ALMET contain more alumina, or different mineral combination of aluminium. So, content of different compounds of aluminium ~45%, like; aluminium nitride, aluminium spinely / spinelide, corindon in ALMET residue suggest that these residues can be use for refractory or fireproof materials. Such materials can be research to recovery aluminium nitride, which is in content ~36%.

Technological residues of FABRIMIXT and GEORGE IMPEX contain more metallic aluminium. That suggests that those two companies have to examine their method to process the aluminium scrap to improve their efficiency. These materials can be turning to account to obtain aluminium sulphate, or aluminium hydroxide, which has different utilizations. The second researches were on possibilitys to decrease soluble salts content from secondary aluminium dross for their recycling.

To establish optimum work parameters and the flow sheet, which are necessary for an efficient technology for removing of the soluble salts from fine fraction of secondary aluminum salt slag, there were sampled salts slag resulted on three platforms with similar profile: ALMET from Năvodari, GEORGE IMPEX from Potcoava, SILNEF from Braşov. The samples were sifted, washed with/without simultaneous grinding, dry and disintegration.

There was studied the washing of the salt slag under many aspects to determine influence of different condition of salt solubilization like, work conditions, number of counter current washing step (one, two, three or four), with or without grinding.
Experiments were made with ordinary laboratory equipment, which was composed by washing vessel with electric agitator, gas bulb, ball mill, aspirator bottle, Buchner funnel, drying cabinet.

The experiments show there are possible to obtain solutions with high content in Na and K in the following conditions: the washing in counter current with grinding in 4th step at 400^0C and ratio S:L = 1:1. The washing with grinding in 4th step offer in the mean time a high fineness of the slag and high concentration of the solutions in NaCl and KCl. The washing efficiency of NaCl and KCl on every step at 20^0C are between 8÷16%, the final washing efficiency after 4 re-pulping being aprox.70% for KCl and 75% for NaCl. The removal of NaCl and KCl from solutions resulted in aluminum slag washing with water, was realized by their concentration by evaporation at the temperature and then the separation of the crystals in two cooling steps at 350C for NaCl and 200^0C for KCl. Finally there was proposed a proper flow sheet, for the counter current washing of the slag salts and conditions to obtain NaCl and KCl salts from the washing solution. The third experiment was to test possibilities to use secondary aluminum technological waste at moulding mixture in foundry for iron heavy casting and to see their influences on solidification processes and on casting parts quality.

There is known that in foundry is used aluminothermy process to maintain high temperature in the mould. The process is based on reaction of aluminium oxidize. In pouring time the iron has 1200-1450^0C, which permits to initiating oxidize reaction of aluminium from mould material. In this way it brings more energy, which maintains the high temperature and permit to pour all the metal with optimal pouring rate. In aluminium dross there are fine aluminium particles, which can be exothermic material and there are metal oxides which have good refractory characteristics because they have high melting point, low coefficient of heat transmission, good temperature stability, etc. These characteristics permit to prevent heat transmission from mould and solidification process is slowly. This process is necessary in pouring iron heavy parts. Aluminium dross granulation is bigger and irregular, while aluminium ashes granulation is smaller and uniform then siliceous sand. These differences can affect row casting surface quality.

The experiments were made in two stages;

- manufacture of the sand mould and watch their behaviour or their changes in time;
- samples pouring and examine surface quality and their porosity.

There were made sand moulds for pouring samples which have form named “Shrinkage cone”. These samples have cylindrical pyramid form with, 70 mm diameter of top and 40 mm diameter of bottom like in figure 2.

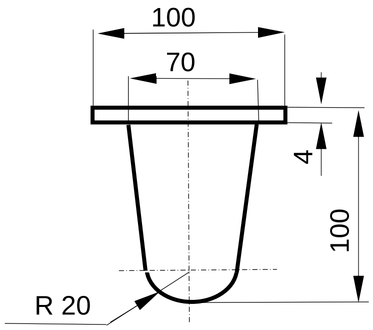

Fig. 2. *“Shrinkage cone” form*

The aluminium dross were mixed with four kind of moulding materials siliceous sand, furan resin, soda water glass and Fortera with proper bonding agent and then the mixture was introduce in sand mould at the contact surface with wood casting pattern. The thickness of layer was from 6 to 10 mm. The experiments of metal pouring were made in two methods: open kind named “direct pouring” and closing kind named “rain pouring”. The samples were watched 48 hours from their manufactured. There were notice the process of chemical interaction between furan resin and components of testing material. For samples with resin furan it was remarked strong reaction between dross oxides and resin components. The experiments showed that the sample of furan resin increase their volume, because of air from chemical reactions. Sand mould with dross present weak tendencies to increase their volume, but sand mould with ashes after 3 hours present important deformations and they cant be use. Fragility of sand moulds permits easy rapping the pattern and easy cleans the cast parts. Thus, the sand moulds with dross or ashes mixed with furan resin can be use in shot time for metal pouring. The samples of sand moulds with dross or ashes mixed with soda water glass and Fortera maintain their form in time, without modification of their forms or dimensions. Some aspects of moulds samples are sowed in figure 3. The experiments show that it is possible to use these furnace wastes in iron foundry, but it is necessary to continue these researches to find the proper ration between components of moulding mixture.

a b c d e

Fig. 3. *a, b - Sample with dross and furan resin; c, d -. Sample with dross and soda water glass and Fortera; e- Samples after 48 hours*

The fourth experiment was to test possibilities to obtain products which can be utilized like coagulants.

The row material, with particle size under 1 mm, was a mixture in equal parts of residual aluminum waste from three platforms. The row material was introduced, for 30 minutes in a perfect mechanic homogenization phase. The experiments were made in two steps: in the first step it was bring in solution of the soluble impurities by washing of the dross with water at the various S:L ratio and temperatures and, in the second step the extraction of the aluminum in sulphuric acid solution like aluminum sulphate. In all experiments was utilized a washing, grinding and dried material resulted by equal homogenization of the dross from those three companies, previous mentioned, with medium chemical composition, show in table 1, and sulphuric concentrate acid, which was diluted with water at desired concentration, function of work parameter which ware established. The experiments were carry out in a laboratory installation composed by: leaching vessel (usually Berzelius glass), with electric agitator, gas bulb, ball mill, aspirator bottle, Buchner funnel, drying cabinet. Firstly, it was calculated the quantity of acid and water of dilution according to chemical composition of the dross. The recipe was: 100 g dross + H_2SO_4

conc. (resulted from calculate) + H_2O (for dilution of the acid). The influence of different parameters on the aluminium release from dross was widely studied in many research aspects, like: the phases contact time was varied between 60÷300 minute; reaction temperature was varied between 80÷1200C; sulphuric acid concentration was varied between 5÷55%; acid excess over stoichiometric necessity; 10, 20% under - stoichiometric; stoichiometric; excess 10, 20, 30, 40 %; S:L ratio was varied between 1:6 ÷1:10; leaching in two steps and leaching in two steps in countercurrent, to decrease the free acidity of the aluminum sulphate solutions; it was varied pH of the solutions.

Table 2. *The composition of the washed, grinding and dried dross, %*

Al	Cu	Mg	Mn	Ni	Pb/ NH_4^+	Zn	Cr	Ca	Ti
39 – 42	0,9 – 1,15	1,5 – 1,8	0,18- 0,21	0,02– 0,04	0,076 / **0,92**	0,9- 1,24	0,02 – 0,04	0,96-1,4	0,2- 0,35
Fe	**B**	**Si**	**Na**	**K**	**Cl**	**SO_4**	**NO_3**	**CO_3**	**F / P**
1,6- 2,4	0,03- 0,04	5,5- 6,7	0,6 - 1,2	0,1- 0,35	0,02-**0,03**	0,1 - 0,5	6,0 - 13	1,6- 2,8	1,3 / 0,033

For all experiments the suspensions were decanting 20 minutes in the mean time with cooling at 900C, filtering at high temperature, washing of the residue with boiled water and drying. The aluminum sulphate solution together washing waters of the residue was analyzed for determination the content of aluminum and the main impurities. The content of anions and cations were determined by: a) - atomic absorption spectrophotometry (AAS or FAAS) and b) - induced coupled plasma spectroscopy (DCP-AES or ICP-AES). To study the influence of the *phases contact time* on leaching efficiency of aluminum, the time was varied between 60÷300 minute. There were analyzed content of aluminum and iron in finale solutions. The results' analyze shows that: the leaching aluminum degree grows in time, especially in the first three hours of the reaction; next to the aluminum are presented, in solutions, many impurities like: Fe, Zn, Ni, Cu, function of the work conditions; sometimes the leaching degree of iron is higher then aluminum; the leaching degree of the iron grows in the first three hours of the reaction then it take place, a re-precipitation of this element from the solution, in time, figure 4.

To study the influence of temperature on leaching efficiency, the temperature was varied between 80÷1200C. The results show that: the leaching efficiency of aluminum grows with temperature at 1100C being 69.84%; the leaching efficiency of iron grows with temperature till 1000C when the values are ≅ 90%, then the values decrease, at 1100C beginning the re-precipitation of iron from the solution, figure 5.

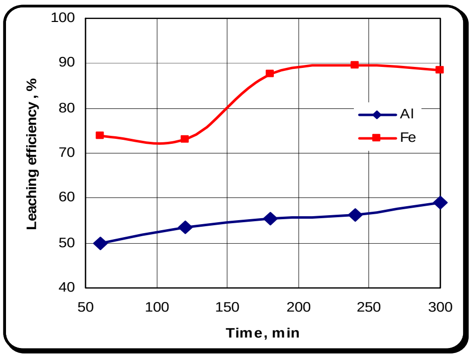

Fig.4. *Variation of leaching efficiency of Al / Fe function of time*

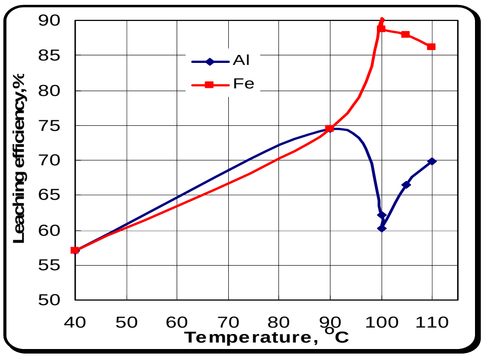

Fig. 5. *Variation of leaching efficiency of Al / Fe function of the temperature*

To study the influence of sulphuric acid concentration on leaching efficiency, for each experiment was utilized: 100 g washed, dried material, like leaching agent sulphuric acid with various concentrations. Work conditions: continuous mixing of the suspension, reaction time 2.5 hours at 85÷900C. The results show that efficiency of leaching aluminum increases from 18.6% to 60.78 % when sulphuric acid concentration increase from 5% to 55 %. Efficiency of leaching iron decreases from 83.3 % to 73.75 % when sulphuric acid concentration increases from 20% to 55 %, figure 6.

To study the influence of sulphuric acid quantities on leaching efficiency for each experiments ware utilized: 100 g washed, dried material, like leaching agent concentrated sulphuric acid with 1.84 g/l density, in the following quantities: 10.20% under-stoichiometric; stoichiometric; excess 10, 20, 30, 40 %. The results show that: the leaching efficiency of aluminum and iron increase till 20 % excess of the acid. In that case efficiency of aluminum leaching achieve 55.6 % and for iron >95%. For 40% excess of acid the leaching efficiency decrease at 52.5 % for aluminum and 81.68% for iron, figure 7.

The experiments of aluminum leaching from the dross have like goal to find the conditions to increase the leaching efficiency of aluminum in sulphuric acid and to decrease the free acidity of the finale crystals of aluminum sulphate. For that, the experiments were realized in one or two steps.

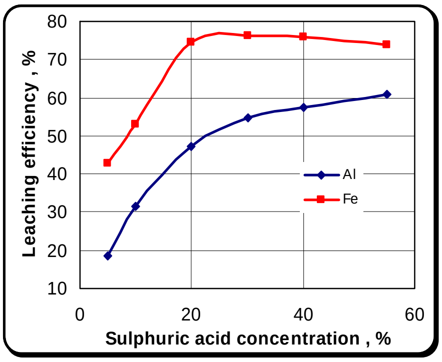

Fig. 6. *Variation of leaching efficiency of Al/Fe function by the sulphuric acid concentration*

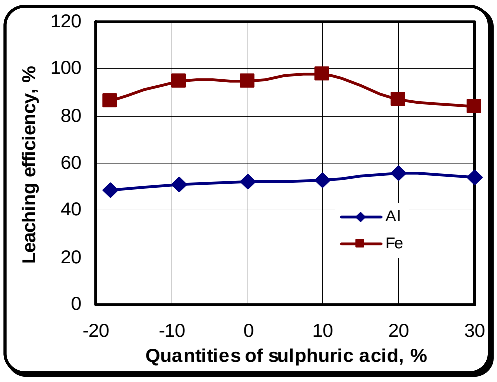

Fig. 7. *Variation of leaching efficiency of Al/Fe function by the sulphuric acid quantities*

The one step, whole quantity of the dross was used with 55% sulphuric acid (under-stoichiometric quantity) at S:L ratio = 1:8. In the second step the difference 45% acid was added over wet solid faze resulted in the first leaching step. It was establish that leaching efficiency on the step is 37.7 / 28.2 % for aluminum and higher for iron 59.11/31.65%. In comparison with the results obtained in the leaching in one step when the leaching efficiency was 56.15 % for aluminum and 89.6 % for iron, in variant in 2 steps it was establish similarly results 55% for aluminum total but 72.7% for iron. To study the influence of S:L ratio on leaching efficiency experiments were realize at various S:L ratio between 1:6÷1:10. The experiments show that at S:L ratio under 1:8, in time, begin crystallization processes of aluminum sulphate from the solutions and the filtration of the suspension is very difficult. To study the influence of pH on leaching efficiency were made experiments with perfect contact fazes, time 2 hours at 950C, at S:L ratio = 1:8, leaching agent sulphuric acid. The results shows that: increasing of sulphuric acid quantities lids to increase of acidity of the solution and at decrease of pH value from 2.13 at 0.36; with increasing of contact time of fazes increase leaching efficiency of aluminum and iron, the consumption of sulphuric acid introduced in reaction, and increase of pH from 1.4 at 2.66.

4. Conclusions

The experiments show that it is possible to use secondary aluminium dross in iron foundry, but it is necessary to continue these researches to find the proper ration between components of moulding mixture. The experiments show that it is possible to obtain products which can be utilized like coagulants from the secondary aluminium dross. The aluminum recovery from dross with high aluminum content is possible to realize with efficiency over 80% in report with soluble aluminum.

The present results establish the bases of a complex, ecologic technology for aluminium recovery from slag with high content of aluminum at coagulants preparation, which have to continue.

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