Research on the Recycling of Pulverulent Waste from the Ferous and Non-Ferrous Industry in Order tu Reduced the Pollution

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Research conducted and presented in this paper have sought to reduce the pollution of the environment by harnessing the red sludge, waste ferrous powdered alumina factories existing areas. The red mud is a waste derived from the production of alumina due to the fact that the raw material bauxite contains besides Al_2O_3 and other minerals such as: hematite, quartz, calcite, rutile titanium dioxide, clay, and shows the red color due to hematite, the whose content can reach up to 45-50% (or 31-35% Fe). Because mineral constituents, containing red mud and water of constitution (approximately 10%). The valorification of red mud in metallurgy is not resolved so far appropriately in terms technical-economical, due primarily to the high content of arsenic than the limit allowed to minerals, which leads to storing it in ponds or throwing by some manufacturers in the sea. This waste has been processed along with other ferrous scrap, are still able powdery or petty, but having a content almost double iron (powder steel mill, mill scale, sludge from agglomeration - furnaces) in order to increase the concentration of iron and decrease the concentration of arsenic by-product.

Keywords : Pollution, recovery of pulp waste, technology

Environmental protection as a European Union member country, is a priority for Romania. In this context, industrial waste is one of the important issues in environmental policy. The waste impact upon the environment has increased alarmingly in the latest years, their uncorresponding administration generating the contamination of the soil and of the ground water and also emissions of methane, carbon dioxide and noxious gases, having direct effects upon the environment. The pulverous and small ferrous residues resulted from metallurgy technological fluxes from, ant's totally recycled. Beside these residues (dusts of steel plants, slurry from agglomeration - blast furnaces, scale, the slag of steel plant - ferrous fraction) can be used another pulverous residues with ferric contents how are pyritic ashes, iron concentrate from thermal power station ashes, red slim, and others [1, 5, 6].

Red mud is a waste resulted from the process of alumina production, as a result of the fact that the raw material - the bauxite - contains alongside with Al_2O_3 other minerals, loo, such as: hematite, quartz, calcite, rutile, small quantities of clay and its red colour is due to the hematite, whose percentage can reach 45-50% (respectively 31-35% Fe). Because of its mineral constituents, the red mud contains constitution water (about 10%). The turning of the red mud to good account in steel making has not been positively solved so far from the technical and economical point of view, the main reason being the content of arsenic, above the acceptable limit for ores. At present it is being deposited in ponds, some alumina producers are even throwing it into the sea.

In bauxite case used-up to the alumina manufacture, the chemical composition fluctuates in the limits: 50-70% Al_2O_3; 0-25% Fe_2O_3; 12-40% H_2O; 2-30% SiO_2 and 2-4% TiO_2. The problem of advantageous manufacture were resold by the chemist Karl Joseph Bayer in 1887 and then within present, this method extensive whole in world, with his help producing almost entire quantity of alumina necessary to manufacture aluminum.

The method is based on the bauxite decomposition, crushed with concentrated solutions of caustic soda to a temperature of as far as 250°C and to a pressure of 40 at, after the reaction:

$$Al_2O_3\text{-}H_2O + 2NaOH = 2NaAlO_2 + 2H_2O. \quad (1)$$

From this process results sodium aluminate solution and residues (in shape of mud), by the name of red slim, withy are deposited on the bottom of the basin and are eliminated after decantation (fig. 1) in ponds.

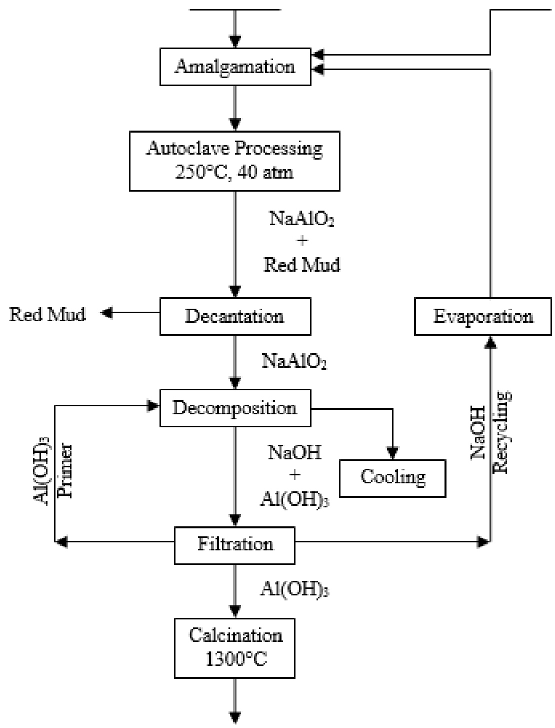

Fig.1. Alumina technological process after Bayer technology

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Arsenic is an undesired element in cast iron or steel, its presence having a negative impact upon the welding characteristics. Inside the blast furnace, the arsenic appears in the form of arsenates, existent in some iron ores, in the agglomerates/pellets, and, as a result of the reduction process, it entirely enters the cast iron and hence the steel. The presence of arsenic in the raw materials is harmful to the metal reserves of a country, considering the cumulative effect of the 10-year cycle of iron re-circulation. Although worldwide there are important reserves of iron ore and ferrous waste containing arsenic, they are not being processed because of the fact that, at present, there are no economically efficient technologies for the removal of arsenic [2].

The in part elimination, because its putting away in the process of the pig iron production is not possible, of arsenic from the processed iron ores out of the furnace (under the shape of agglomerated materials, briquettes, pellets) presents a special importance, because by researches and experimentations, there can be reached to the technological solutions of ferrous with arsenic raw materials rendering valuation. During the process of agglomerating/ burning of the pellets, starting from 400°C, arsenic combinations are oxidized to the shape AS_2O_3 (trioxide of arsenic). On the temperatures of over 450°C it is volatilized and passed into gas status, where in the presence of ferrum oxides and in oxidizing medium, it is oxidized continuously to penta-oxide (AS_2O_5), which is not volatile and is dissociating only at high temperatures (700 - 1000°C) and in the reducing atmosphere.

Under this shape, a part of arsenic remains in the processed material (agglomerated material, pellets), becoming cold once with that one, and in the presence of oxide of calcium, the penta-oxide of arsenic, oxide of arsenic forms the arsenate of calcium, that, also, is a stable component.

In spite of the unfavorable conditions, during the regular agglomeration/ pellets burning process, up to 25% of the arsenic initially contained by the ore (respectively in ferrous pulverous residue) can be eliminated. The use of high temperatures for the agglomeration/ pellets burning process favors a higher removal of arsenic. The agglomeration (pellets' burning) in a more reducing atmosphere (possible in rotary furnaces) leads to a percentage of amount 50% of the arsenic eliminated from the charge.

Based on the results of laboratory testing, research and experiments carried out in this work, watched the development of specific technologies for processing red mud powder together with other waste. The particularity of these technologies will be that will help to reduce the arsenic content in the product (agglomerated, pellets, briquettes) to the permitted limits for processing these residues in metallurgy [3].

Experimental part

Experimental research aimed at establishing opportunities to exploit the resulting red sludge from alumina production, currently stored in sludge beds. For alumina production was used as a raw material bauxite average chemical composition shown in table 1.

The chemical composition of red slim, resulting from alumina production is presented in table 2 and the granulometric composition in table 3.

It was considering that it is presenting an interest the experimentations in the phase of laboratory, the processing of the red mud by pelleting. Having in the view relatively

Table 1
AVERAGE BAUXITE CHEMICAL COMPOSITION

Component	Al_2O_3	Fe_2O_3	H_2O	SiO_2	CaO	MgO
Content, [%]	55.5	24.1	13.2	6.0	0.8	0.4

Table 2
RED SLIME CHARACTERISTICS

No.	Assaying elaborate	Measurement units	Slam from sludge bed
1	pH		8.5
2	Aluminium (Al)	%	4.86
3	Arsenic (As)	%	0.001
4	Nickel (Ni)	%	0.0036
5	Zinc (Zn)	%	0.0053
6	Magnesium (Mg)	%	0.2
7	Titanium (Ti)	%	1.12
8	Vanadium (V)	%	0.092
9	Iron (Fe)	%	30.44
10	Calcium (Ca)	%	3.24
11	Natrium (Na)	%	3.0
12	Alkaline earth carbonates	%	0.8

Granulometric class	<63 µm	63-100 µm	100-250 µm	250-500 µm	500-710 µm	710-1000 µm	>1000 µm
Quantity, [%]	54.15	15.84	12.10	7.44	7.34	3.13	0

Table 3
RED SLIM GRANULOMETRIC COMPOSITION

Table 4
MATERIALS CHEMICAL COMPOSITION, USED IN PELLETIZING PROCESS

Component	Chemical composition, [%]											
	FeO	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	MnO	As	Alkaline oxides	Alkaline earth carbonates	Others components	Cal. Loss
Steel plant dust	1.56	90.04	0	1.24	0	0.26	0.46	0	0	0	7.44	0
Red slime	0	48.50	9.94	15.22	1.80	1.94	0	0.001	5.23	3.309	4.06	10
Slam agglomeration-blast furnace	7.13	26.45	1.11	8.41	17.6	7.21	8.43	0	0	0	23.66	0
Betonite	0	0.7	0.3	3.3	0.4	0	0	0	0	0	95	0.3
Lime	0	0.4	0.55	0.7	96	1.3	0.2	0	0	0	0.85	0

Fig. 2. Crude pellets

Fig.3. Burned pellets

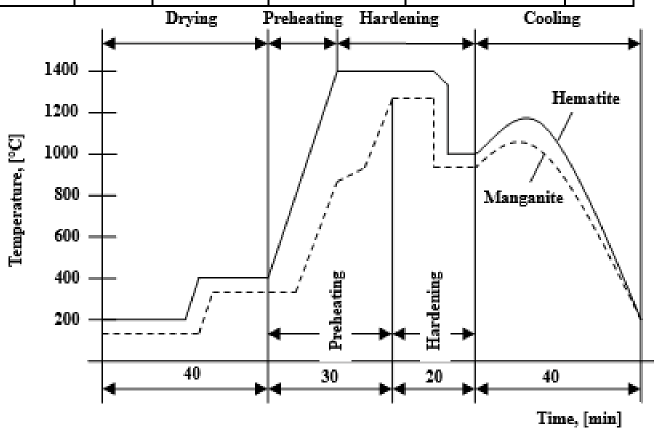

Fig. 4. Pellets burning diagram

low content of ferrum, as well as the content of arsenic (but this does not exceed the limit that is admitted for the iron ores) was processed this assortment of raw material - together with the dust of electric steel works and slag of agglomerating-furnaces (carbon will assure a reducing of the oxides of ferrum and will contribute to be obtained a reducing atmosphere at the pellets burning) [4]. As bonding agent we used bentonite and lime. The processed material chemical composition is presented in table 4.

The palletizing was carried out in the laboratories of UPB. The experimented waste materials have had a proper conduct during the process of pelleting. On the final part of pelleting there was introduced graphite dust into the plate of pelleting, which ensured for the pellets an external cover riched in carbon, and in such a way the pellets are not glued together (fig. 2) and, also, during the burning they contribute to be obtained a reducing atmosphere and for to be putting away a part of arsenic with the wave of gases. The obtained pellets were the hardening (burned) (fig. 3) in the Nabertherm furnace (maximal temperature 1750°C), using the diagram from figure 4 [4].

Results and discussions

Chemical composition of the raw pellets is presented in yable 5.

Burned pellets chemical composition is presented in table 6.

The compression strength of the hardened pellets are shown in table 7.

The analysis results can be observed that the compression strength, where the 5 recipes experimental ranged between 218.6 -224.1 daN / pellet.

- These values confirms the possibility of using the pellets obtained in electric arc furnaces load, we are recommended a minimum compression strength of 160 daN/pellet.

- The highest compression strength of 224.1 daN / pellet obtained if the recipe comprises R1 which had the highest content of Fe_2O_3 (the 66.33%), the lowest content of Al_2O_3, SiO_2, CaO, MgO, of alkaline oxides, alkaline earth carbonates and arsenic (from 0.000117%).

- The lowest compression strength of 217.1 daN / pellet obtained if R4 recipe that was composed lowest content of Fe_2O_3 (the 58.954%), the highest content of Al_2O_3, SiO_2,

Table 5
ROW PELLETS CHEMICAL COMPOSITION

Recipe	Chemical composition, [%]											
	FeO	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	MnO	As	Alkaline oxides	Alkaline earth carbonates	Others components	Cal. Loss.
R1	2.02	65.32	1.69	4.51	6.80	1.55	1.53	0.00016	0.78	0.51	13.36984	1.92
R2	1.92	63.27	2.17	5.23	6.88	1.65	1.52	0.00021	1.05	0.65	13.63979	2.02
R3	2.08	59.56	2.23	5.43	8.39	1.84	1.76	0.00021	1.06	0.66	15.00979	2.02
R4	1.98	57.50	2.71	6.15	8.46	1.94	1.72	0.00027	1.33	0.82	14.51973	2.52
R5	2.28	61.68	1.64	4.74	8.61	1.90	1.93	0.00014	0.75	0.45	14.50086	1.42

Table 6
BURNED PELLETS CHEMICAL COMPOSITION

Recipe	Chemical composition, [%]										
	FeO	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	MnO	As	Alkaline oxides	Alkaline earth carbonates	Others components
R1	2.042	66.330	1.711	4.586	6.902	1.577	1.564	0.0001170	0.802	0.502	13.08238
R2	1.555	64.833	2.234	5.344	7.058	1.678	1.557	0.0001577	1.079	0.677	14.18448
R3	2.060	60.821	2.266	5.561	8.561	1.887	1.788	0.0001571	1.075	0.675	15.30585
R4	2.071	58.954	2.785	6.301	8.691	1.981	1.775	0.0001973	1.348	0.847	15.24680
R5	2.330	62.413	1.666	4.787	8.726	1.912	1.968	0.0001090	0.744	0.470	14.76389

Table 7
COMPRESSION STRENGTH OF THE HARDENED PELLETS

Recipe	Compression strength, [daN/pellet]										
	1	2	3	4	5	6	7	8	9	10	Average
R1	211	208	223	205	239	247	203	242	208	255	224.1
R2	213	222	209	194	242	237	198	239	215	218	218.7
R3	203	199	217	227	218	233	228	238	213	210	218.6
R4	195	215	208	241	232	219	208	218	222	213	217.1
R5	236	217	243	230	212	208	230	246	204	206	223.2

CaO, MgO, of alkaline oxides, alkaline earth carbonates and arsenic (from 0.0001973%).

Conclusions

Analyzing the results of researches made, the following can be concluded:

From the qualitative point of view, the red mud is corresponding to the conditions imposed to the process of pelleting and can be rendered valuation nearby the other pulverous waste materials.

By processing the waste materials used within the experimentations, does not matter the receipts proposed for the experimentation, there have been obtained the proper pellets, proper from the point of view of the resistance to the compression and chemical and granulometric composition.

The grade of arsenic elimination has been comprised between the limits 24.90-33.16% (an average of 30%).

In view along with the degree of removal of arsenic and arsenic content, that further research on harnessing interest in steel red sludge.

The pellets obtained can be used in loading electric arc furnace.

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