Obtaining of titanium, minor and rare earths elements by solvent extraction, during complex processing of high silica bauxite

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The continuous research for developing of economical technologies for processing of high silica bauxites, led to a complex process suitable for the exploitation of almost all ingredients in this bauxite. This process consists in the smelting of bauxite burden, enriched with the sintered or pelletized material with high iron content in electric furnace, and production of an alloy or pig iron and the slag. The slag is then leached with diluted sulphuric acid, after that is undissolved part of slag converted to a synthetic fertilizer. From the pregnant acid solution are extracted almost all components by solvent extraction. In this paper, author outlines the conditions of processing and the results obtained.

1. INTRODUCTION

It is a well known fact that there are large occurrences of bauxite, characterised by high SiO_2 content, which are not suitable for alumina extraction treatment by Bayer process. A major part of these bauxites also contain considerable amounts of Iron compounds, so that they simultaneously represent some type of poor iron ore.

During the treatment of such bauxites, with the view of exploiting the iron compounds contained therein, often a slag is obtained which, with other components, contains soluble binary calcium aluminates that could be separated from the primary mass of silicates. This attracted attention so that at many places in the world, works were conducted on the treatment of ferruginous and high silica bauxites with the view of producing special quality pig iron or ferro alloys and soluble alumina slag.

Yugoslavia also has considerable reserves of bauxite, which are not suitable for treatment for alumina by the Bayer's process. As those bauxites usually contain high percentage of iron, the problem of their treatment for producing pig iron and soluble aluminate slag has been well analysed. In the case we use high silica bauxite with few percentage of iron, the addition of iron scrap to burden solves the problem.

The extensive long term, industrial scale investigations in Yugoslavia, are shown that the commercial success of the smelting of high silica bauxite, will, depend on finding solution for the utilization of the slag obtained by smelting, other than as ingredient in portland or alumina cement or lightweight construction aggregate or even for producing of alumina.

Extensive investigations, including the large scale pilot plant work done in the blast and electric furnace, led to a complex process suitable for the exploitation of almost all ingredients of bauxite, consists as follows:

2. PRACTICAL WORKS

This works consists in the large scale smelting of the bauxite burden in the blast and electric furnace, to produce an alloy or high quality pig iron and the slag. The slag was then leached in pilot plant with diluted sulphuric acid, after that is undissolved part of the slag converted to a synthetic fertiliser. Finally, the large laboratory scale solvent extraction was used, for the extraction of the useful ingredients from the pregnant acid solution.

2.1. The smelting of bauxite

The bauxite burden, enriched with the sintered or pelletized material with high iron content, or with iron scrap, was melted in both, the blast furnace and electric furnace on an industrial scale. The smelting process must be carried out in such a way that titania go to the slag, as well almost all zirconia, thoria, uranium, minor and rare elements, except the vanadium, niobium, chromium and molybdenum, which are reduced to the pig iron. Particular attention should be paid to the reduction grade of titania; 0,3 percentage of titanium in the pig iron made no difficulties in the smelting process.

The resulting pig iron was of high quality, mostly foundry iron, norwegian VANTIT — type, with about 3 % Si and very low sulphur. The reduction degree of titanium, vanadium and chromium into the pig iron, depends also of the slag basicity, as follows:

	Basic slag (%)	*Acid slag* (%)
Vanadium	77,00	95,00
Chromium	83,90	94,00
Titanium	11,3	5,00

It is normal to expect that the smelting of bauxite in electric furnace has certain advantages from the point of view of temperature regulation, work with aluminate slag, fuel consumption etc. Low fuel consumption would also results in production of slag with lower SiO_2 content, which is either not possible or it is very difficult to obtain in the blast furnace.

Under average conditions and the average data for a Tysland-Hole furnace, type Siemens-Demag, 10.000 kW rate, with the normal production of 100 tpd of pig iron, for the smelting of prepared bauxite burden is shown in Figure 1, which illustrates the flow sheet for this smelting.

During the first years of systematic works on the smelting of bauxite in Yugoslavia, our works was the same as the works in the other countries over the world. The slag produced by these smeltings was used for production of alumina like to the works in Germany, France and USSR and in other countries, then for the titanium ferroalloys, and, also for the production of the high quality cement and lightweight construction aggregate.

Later, because of the economical reasons, we found that the commercial success of the bauxite smelting will depend on finding a better solution for utilization of the slag produced by smelting, other than the solutions mentioned above.

By the works done in Yugoslavia was found that in order to get this commercial success one of the most attractive solutions is the complete exploitation of the slag produced by smelting of bauxite, including here all of its useful ingredients like titania, zirconia, alumina, iron, uranium, thorium, lanthan, scandium, ytrium, europium etc. The rest part of the undissolved slag can be finally converted to a synthetic fertilizer similar to the ground basic slag.

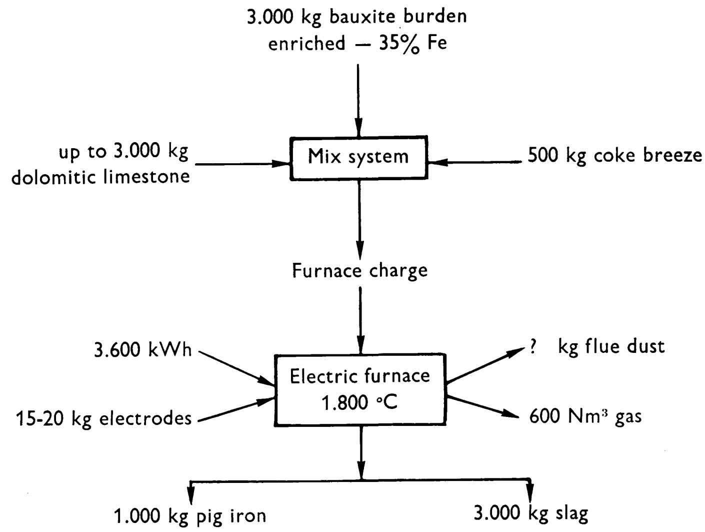

Fig. 1. — Flow sheet of electric furnace smelting process

3. LEACHING OF THE SLAG

The slag obtained by the smelting process is granulated with water during the tapping period. The granulated slag is then conveyed into a tank which is strongly agitated and which contains sulphuric (30%). The slag: the liquid ratio is 1:6. The addition of the slag raises temperature to 80-90 °C, as a result of the heat of dissolution a part of the slag. After a total of 30-60 minuts — depending on the slag composition — the muddy liquid is sent to solid mud separation.

This separation (filtration) is characterized by the fact that it must be carried out with a surplus of sulphuric acid in the solution in order to prevent the hydrolizing of the dissolved titanium. Such reaction is of great importance so long as the solution is in contact with the undissolved slag.

The consumption of the sulphuric acid is between 900-1.285 kg/ton of slag, what depends of the slag basicity.

The separated slag in the quantity of about the same as original slag, because of $CaSO_4$ created by leaching process, is used without washing for the production of a new type of synthetic fertilizer, similar or better to say somewhere between the ground basic slag and superphosphate, which, by name of "PELOFOS" has found usage in the agriculture in different countries (Yugoslavia, Czechoslovakia and India). The little sulphuric acid content, as well as the rest of sulphate of elements contained in the original slag and now adsorbed in the solid residue, react with the tricalciumphosphate part of the raw phosphate rock, fine grinded, added to the mixer in appropriate proportion to the solid slag residue, in such a way as to produce a fertilizer with microelements in sulphate form. The ratio solid slag residue: raw phosphate is about 45: 55, in order to produce a fertilizer with 17-18 percentage of P_2O_5 content. This fertilizer is of the same or even better quality than superphosphate, especially for the acid soils.

The chemical composition of different slag types is shown on the Table I.

TABLE I

Sample	SiO_2	TiO_2	Al_2O_3	FeO	MnO	CaO	MgO	S
I	14,68	2,59	47,28	1,14	0,29	31,89	1,43	1,15
II	14,02	1,78	49,68	1,18	0,24	31,00	1,68	1,02
III	19,32	2,77	41,11	2,00	0,71	30,93	1,95	1,11
IV	19,73	1,82	35,12	1,17	0,34	39,89	1,11	1,04

Figure 2 illustrates a possible flow sheet for the leaching of the slag obtained by smelting of bauxite.

Solvent extraction of the acid — water pregnant liquid.

The clear, pregnant acid solution, after the undissolved slag filtration, is sent to the mixer-settler department for the solvent extraction operation. This operation proceeds

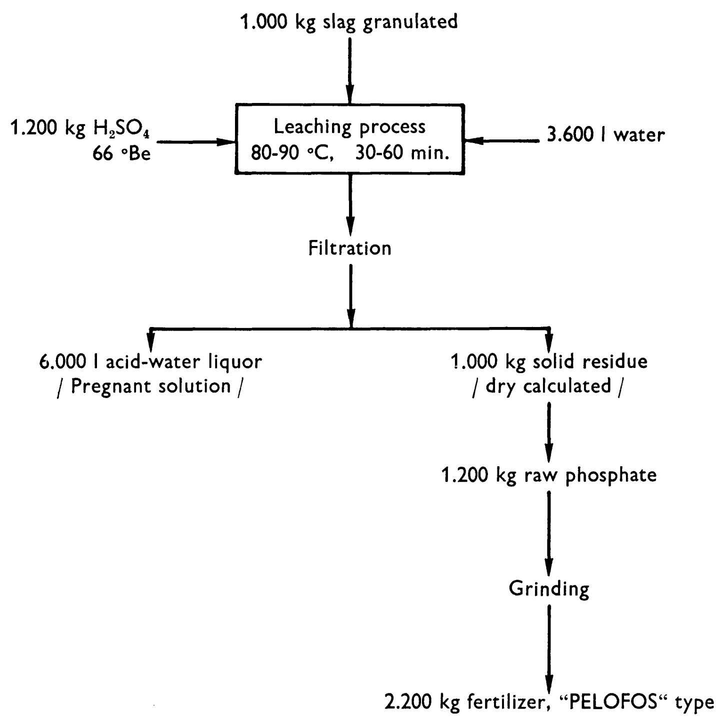

Fig. 2. — Flow sheet of leaching process

favourably when the acid solution is treated at the certain concentration with the counter-current organic solvent. Therefore the pregnant solution must be diluted with water, on the way to mixer-settler department. The diluted acid-water solution contains

Al_2O_3	6-8 g/l
Fe_2O_3	3-5 g/l
TiO_2	0-1 g/l

For the solvent extraction process was used Kerosene with 5 percentage of Di-2-Ethylhexyl-phosphoric acid (DEPHA) with some 2-Ethylhexanol. In the industrial level trial work the water-acid solution: organic phase ratio was 1,6: 1. Solvent losses have been held to less then 0,02 percentage of the raffinate volume. Generally it is confirmed that an overall loss of 0,05 percentage or less can be maintained.

The first step of mixer-settler solvent extraction — at pH below 1,0 — takes a very short time and at the end practically all TiO_2, ZrO_2, ThO_2, uranium, lanthan, scandium and ytrium from the acid-water solution are extracted to the organic solvent liquer. The organic solvent liquid is then stripped with Na_2CO_3 dissolved in water to a 10% solution, with the optimal ratio of 5: 1, after which the organic solvent liquid is sent back to reuse in the solvent extraction operation, practically without loss. $Ti(OH)_3$, hydrolized from the Na_2CO_3 — solution is filtered with a normal vacuum filter, either on the fixed or belt type, dried and calcinated to TiO_2. The yield of TiO_2 based on the total TiO_2 content in the slag ranges from 85 to 90 percentage. The clear Na_2CO_3 — solution is sent back to reuse in the stripping process, until its ZzO_2, ThO_2, uranium, lanthan, scandium, ytrium and others content reach the concentration level for their commercial production, and, finally, the pregnant Na_2CO_3 — solution must be replaced with a new one. The acid-water solution, after first step of solvent extraction, contained almost the same quantity of Fe_2O_3 and Al_2O_3 but traces of TiO_2, ZrO_2 and others elements, is treated with lime or with soda ash to pH.3, and then is sent to desilication at atmospheric pressure.

The desilication operation takes about two hours and at the end it is possible to separate by filtration a mud consisting of calcium-aluminium silicate or sodium aluminium silicate, with about 3-4 percentage of Al_2O_3. After the separation of this mud, to the clear solution is added new portion of NaOH to increase pH to a level between 3,5-4,5 for the precipitation of $Fe(OH)_3$. This precipitate is then separated by filtration on the same way as TiO_2.

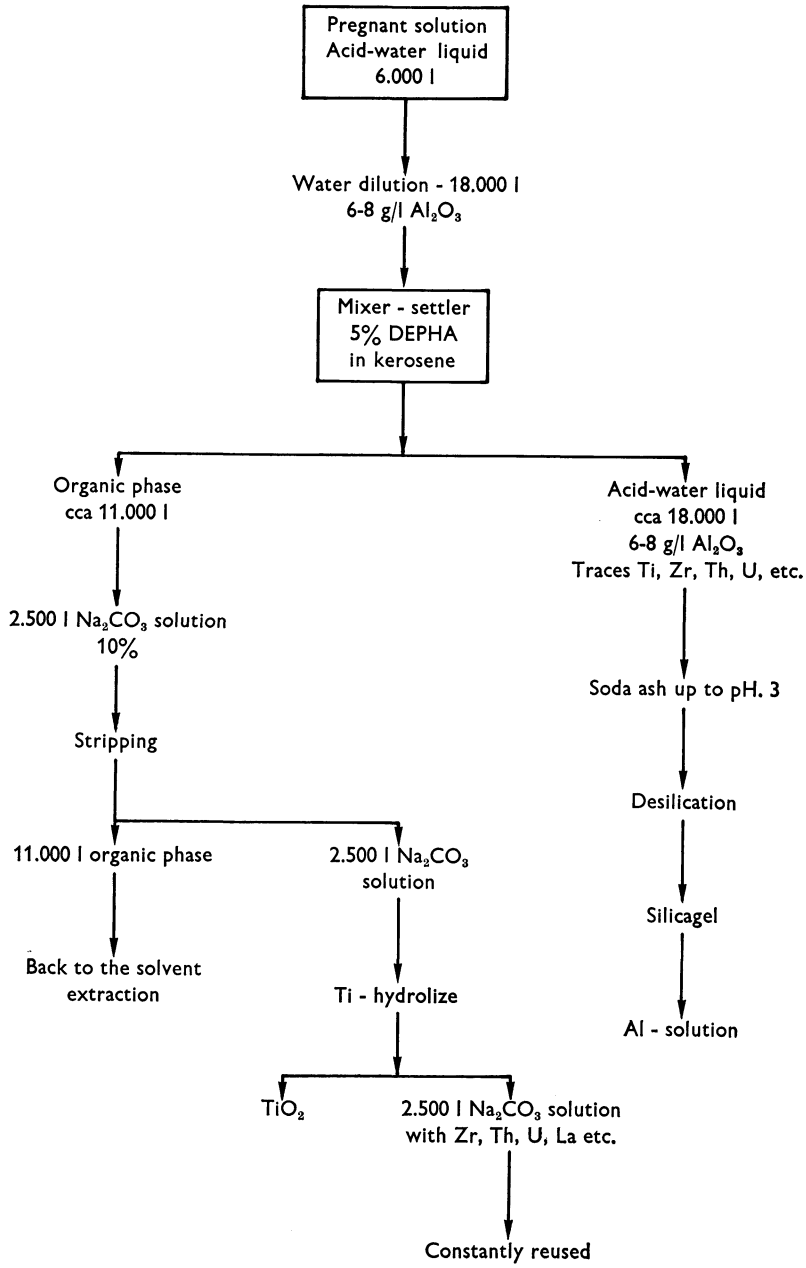

Fig. 3. — Flow sheet of solvent extraction process

The aluminate solution, provided this operation has been carried out in accordance with the directions give above, hases SiO_2 and Fe_2O_3 content less than 0,5%. With further addition of NaOH can be reached pH . 5,0 and precipitated a complex aluminium sulphate salt which can be transformed to aluminium sulphate, $Al_2(SO_4)_3 . 18\ H_2O$ or calcinated to Al_2O_3.

The extraction yield of alumina, based on the total Al_2O_3 content in the bauxite and the slag, ranges between 85-90 percentage.

The waste liquid after the extraction and filtration of Al-precipitate can be used for the recovery of sodium sulphate, only if a very cheap steam is available.

Figure 3 illustrates a possible flow sheet for the processing of the clear acid-water solution obtained by leaching of the slag, by a solvent extraction process.

4. CONCLUSION

The extensive long term laboratory and industrial scale investigations in Yugoslavia, shows that the smelting of bauxite with high silica content, enriched with the sintered or pelletized material or with iron scrap, can be done technically correct especially in the electric furnace. The commercial success of the smelting, meanwhile, will depend on finding solution for utilization of the slag obtained by smelting, other than an ingredient in portland or alumina cement or lightweight construction aggregate.

By these works was found — from our point of view — that in order to get this commercial success, one of the most attractive solution is the complete exploitation of the slag produced by smelting of bauxite.

The complex utilization of such a quality of bauxite in our process is characterized in smelting of the burden enriched with iron on the way mentioned above, in an electric furnace, Tysland Hole type, in order to produce high-quality pig iron VANTIT type, and the slag suitable for production of titania, alumina or their compounds, as well as the zirconia, uranium, lanthan, scandium, ytrium and other minor elements and rare earths.

By the acid treatment of the slag produced, all useful ingredients of the slag can be obtained by solvent extraction process, and the solid slag residue then converted to a synthetic fertilizer of the quality same or better than superphosphate, well known in the agriculture praxis of Yugoslavia, Czechoslovakia and India.

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