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THE BAUXITE WASTE TAILINGS (Issues and Management) Kingston, Jamaica, 26 - 30 October 1986

A NEW APPROACH TO ECONOMIC UTILIZATION OF BAUXITE RESIDUES

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This paper has been prepared without formal editing.

l. Introduction, development and application of the new approach:

On the basis of knowledge and experience collected in working with ceramics technologies, a system and method were developed to utilize large amounts of red mud in the production of ceramics. According to the Hungarian patent No. 171.820., a multi-component system can be applied permitting to increase the content of dry red mud up to $90\quad$ X in the dry ceramic mixture. This mixture yields upon firing at relatively low temperatures of 950 to 1150 °C a diverse line of high strength products, such as heat insulating bricks, heat insulating water pipes, building bricks, wall and floor tiles, low weight building materials (specific weight 1 t/mJ}, brickwork of foundries, surfacing materials. The additives are, in majority, wastes or refuses of other industrial branches constituting environmental problems themselves at present, e.g. flotation refuse of ore dressing, sand washing sludge, waste of plants of silicate industry and their dust, mining refuse of igneous rocks, oil shale slag, refuse of perlite grinding, dust of perlite swelling, ashes and flue dusts of power plants, loess, dolomite, diatomaceous earth, household and industrial scrap glass, zeolite, quartz sand, sandy illite refuse, etc. By proper selection of quantity, quality, grain size of the additives and of the manufacturing technologies, chemical and physical properties of the bulk and surface, technical characteristics of the end products may be optimized. Frost-resisting ceramics may also be produced. Red mud is not easily transportable in original state, however, if it is processed to mixtures at the alumina plant, it can be transported to the ceramic factories of building materials and heavy ceramics. 3y applying this techn~logy the total quantity of red mud released by alumina production could be processed to valuable building materials, ceramic and other products in the majority of countries processing bauxite.

The new method was patented in Britain, Australia, the United States and a number of other countries. It was first published internationally in outline at the UNEP/UNIDO Conference on Enviro.mental Protection for the Alumina Industry held in Paris in December 1980 and it was included into the list of recommendations adopted by the Conference. Based on this recommendation, the Jamaican Government requested first through UNIDO the preparation of a special study applied to the conditions prevailing in Jamaica.

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The Indian state company, Sponge Iron India Ltd was the second for whom upon the request of the Governaent of India to UNIDO an application study with pilot-scale testing was elaborated in 1983, demonstrating the possibility of utilization of ore washing and gas washing sludges of a steel plant, with compositions similar to red mud, for building industrial purposes.

In 1984, the Chinese Government requested a similar study to be organized and financed by UNIDO on the elaboration of a process for the economic utilization of the so-called brown mud residues of the Shandong Aluminium Works for building material purposes.

In 1985, the Indian Government requested UNIDO again, now for the Indian Rare Earth Company, Bombay, to elaborate economic solution for the utilization of garnet sand, based on the same technological know-how. In the same year and along the same line, a study was elaborated for the Korba plant of the Bharat Aluminium Company, India, for the utilization of their red mud for building material purposes.

In Hungary, one of the alumina plants will be expanded to produce mixtures from red aud. This mixture will be suppliad to a ceramics factory to produce 150.000 m^2 /year ceramic tiles and 50 million pcs per year of klinker bricks. In case of conversion of the brick and ceramics industry ~f Hungary, to process such mixture, the total volume of Hungarian red mud of one million tons per year could be processed without fully meeting the raw materials need of the ceramics industry.

In the following, the most frequent oxides and minerals occuring in the metallurgical wastes are shown.

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of occurence: $\Delta\mathbf{1}_2\mathbf{0}_3$: Bentonite (montmorillonit) CaAl₃ [SigO₂₀(OH)₄].nH₂O lllit (hydromuskowit) KAln [Si7AlO₂₀(OH)4.nH₂O Kaolinit $\text{Al}_2(\text{OH})_4$ Si₂0₄ Gibbsite $\Delta l(OH)$ 3 $(\Delta l_2O_2.3H_2O)$ Boebaite **AlOOH** $(A1_20_3.H_20)$ Diaspore $A100B$ $(A1₂0₃, H₂0)$ Alumogoethite Fe(Al/OOH) with isomorph substitution Sodiua-aluainiua silicates (sodalites), NAS $3(Na_20.Al_2)$ 3.2SiO₂)Na₂X.nH₂0 where X may be CO^{2-} SO^{2-} $OH^ AlO^-$ Calcium-aluminium silicates, CAS Tri-calcium aluminate $3Ca0.A1_20_3.6H_20.$ $Fe₂O₃$ Ilmenite PeTiO₃ Hematite $Fe₂O₃$ Geothite FeOOH Magnetite $Fe₂O₃$. FeO Pyrite $res₂$ Marcasite r_{res_2} Garnet (almandin) Fe3Al2 (Si3012) $$10₂$ Clay minerals (kaolinite, montmorillonite, illite) $Quartz$ $510₂$ Sodalites NaS Calcium-aluminium silicates, CAS

2. Review of main oxide constituents of heavy ceramics and their form

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TiO₂

$Na₂O$

Sodalites, NAS Sodium titanates Other soiwa salts

MgO

CaO

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 v_2 ^o₅ $Ca(VO₃)₂$ Calcium-metavandate Other vanadium containing minerals

 $P₂O₅$

Phosphorite Apatite $Ca_3(PO_4)_2$ $CA_4[(PO_4)_2F]$

 $CO₂$

Mainly in the form of calcite and dolomite

 $SO₃$

In the form of various minerals (alunite, sodalite, pyrite, etc.) P; Mainly in the form of apatite and fluorite C; in the form of various organic substances.

L.O.I. Crystalline water of minerals decomposed up to 1.100°C. Thermal decomposition of $CO₂$, $SO₂$ and organic substances.

3. The new compositions applied:

The maximum $Fe₂O₃$ content of the so-called klinker clays of high Fe 203 content used in the ceramic industry has been 11 p.c. According to the technical literature materials of higher $Fe₂O₃$ content cannot be used for this purpose from technological point of view. This statement relates of course, to the traditional clay based ceramics production.

The author investigated and found that in spite of the high iron oxide content it is possible to produce better quality products from the metallurgt~al vastes and by-products than those made of classical silicate type industrial raw materials. The elaboration of the suitable optimum technology requires the chemical and mineralogical analysis and investigation of the high iron content metallurgical wastes. In addition, local availability of mining and other industrial wastes and by-products of high silicate or silica content is also necessary. In the possession of the composition data the next step is the optimization of

the aaterial composition and of the technology of production of the product. On the basis of the initial data received an optimum composition for the manufacturing of architectural ceramic products was worked out, peraitting application of single-firing technology.

The optimum composition of a final ceramic product is reflected by the following percentage figures:

In the Table No.l, the oxyde composition of different metallurgical wastes and by-products is shown to demonstrate the extent of deviation from each other ond from the optimum mixture.

In the following, examples of the initial chemical composition of some metallurgical wastes are shown against the final composition optimized for products manufactured from them within the scope of UNIDO projects.

Table 1: Chemical analysis of muds, sludges, and waste materials of high iron oxide content --

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 $\mathcal{L}_{\text{max}} = 0$

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 $\sim 10^7$

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SiO ₂	iron ore washing sludge 50, 6Z	gas washing sludge 20,0.7	optimized brick composition $50 - 55x$
Al ₂ O ₃	13,0	13,9	$13 - 20$
Fe ₂ O ₃	20, 9	53,6	$15 - 25$
TiO ₂	1,8	1,5	1,2
Mg ₀			0, 5
CaO ÷.			$1 - 2$
L.0.L.	4,7	1,9	

Indian steel plant sludges (Sponge iron of india Ltd. Kothagudem)

Indian garnet sand (Indian Rare Earth, OSCOM Plant)

4. Application of energy - saving technologies:

As a result of the first project carried out based on the classic double- firing techrologies for the Jamaican Bauxite Institute in 1982, it transpired that without the elaboration of cold technological processes with low energy consumption the chances of application in countries poor in energy resources are low. At that time there was no request from Jamaica to continue with improved approach. In 1984, however, the Chinese Shandong Aluminium Works turned to UNIDO to help them to elaborate a low energy consumption programme for the economic utilization of their brown mud generated from alumina production based on series-combined Bayer technology. In implementation of the relevant contract concluded with UNIDO an energy sa ing single-firing technology was elaborated for the munfacturing of glazed floor and wall tiles, and a cold manufacturing technology for production of heat insulating foamed gas silicate blocks and bricks from the brown mud was developed. The single-firing manufacturing technology of producing glazed floor and wall

tiles with a bulk density of 1,2-1,5 g/cm^3 is a new technique unique all over the vorld, resulting in a 40 % saving in energy as compared to the double or triple firing techniques usually required for the same purpose due to the requirements of mechanical strength of the tile material, its surface quality and esthetic appearance.

It is to be pointed out that this newly elaborated technology applied to the Chinese brown mud based floor and wall tile production results not only in the significant saving of energy, but also decrease of other wastage, better control of the process and smaller investment costs in comparison to the traditional clay mineral based production technology.

Later on, in the first half of 1986, this new techology was adapted within a new UNIDO project on red mud utilization for India with the same good results, described in the final report of the project, submitted through UNIDO in September this year.

5. The example of *ted* mud of Korba Alumina Plant India

Economic calculations for the establishment of a proposed tile plant for 2 different capacities.

5.1. Unglazed single Fired Floor and Wall Tiles for red-mud technology for Industrial Use /Predesign estimate/ Annual capacity 150 000 squ

A. Site, buildings, etc.

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B. Utilities

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8.· Subtotal

2,539,500

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 \mathbb{Z}^2

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5.2. Glazed and decorated tiles for red-mud based technology /Predesign estimate/ Annual capacity 2,000,000 sqm, Single fired Floor and Wall Glazed Tiles

Glazed and decorated tiles /Profitability/

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Glazed and decorated tiles /cash flow at Rs. 100/sqm./

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- 3. Annual repayaent of loan principal of Rs. 1000,000, in 7 years 4. Net cash flow /1+2-3/in any production year 14,000,000 43,355,600
- 6. The example of brown mud of the Sbandong Aluainiua Plant, People's Republic of· China:

Since details of the new compositions are at present under patenting procedures, only the case of brown mud of the red mud sintering branch of the series-complex process, applied at the Sbandong Plant in China can be briefly described here.

The production of alumina in the Shandong Aluminium Work is carried out by the series-combined Bayer process and the recovery of the chemically bound caustic soda and alumina formed during the digestion of high silica bauxites is achieved by sintering of the bauxite residue with soda ash and limestone at 1.100 to 1.200 °C to generate calcium silicate and sodium aluminate.

This reaction ls given by the following equation.

¹

The calcined product is ground and leached with dilute aluminate liquor to recover its sodium and alwaina values.

The calcium silicate which residue is used partly to manufacture Portland cement and it is partly discharged to impoundment lakes.

The CaO content of brown mud is bound partly in CaCO3 while the other part may be found primarily in dicalcium-silicate $(Ca2S10)_4$ subordinately in . sodalite (sodium-aluminium-silicate) and in genlenite $(2Ca0.A1₂O₃.Pe₂O₃)$.

The Al_2O_3 is divided between the sodalite and the gehlenite approx. fifty-fifty per cent. Tbe iron is bound to gchlenite, and other iron gels. On the derivatographic curves, the DTA indicates this state of iron by an elongated exotherm peak between 100-400 °C.

The exothermia beginning on 800 $^{\circ}$ C shows the decomposition of CaC03 and the polimorf transformation of dicalcium-silicate. Grain size distribution of the natural (dry) material is as follows:

- a) bigger than 2 mm is 58 X
- b) between $1-2$ mm is 24×7
- c) less than $1 \text{ mm is } 18.7$

The CaCO₃ content of the fractions above 2 mm, is between 30-36 \bar{x} that of the fraction below 2 mm is between $25-30$ λ .

Grain size distribution of the soaked mud is as follows:

a) Results of manufacturing of glazed floor and wall tiles on pilot-demonstration scale:

The main oxyde components of the Shandong brown mud together with that of the floor - and wall tiles made from optimized mixture $(40 \t X$ brown mud and 60 % of bauxite clay, sandstone and mining refuse) after firing is shown in Table 2.

The technological sequence of floor and wall tile manufacturing is shown in comparison below:

Traditional technology

Raw material: different clay sorts, quartz

Additives: sand, dolomite, limestone flour,

feldspar

Storage

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Measuring

Grinding

Homogenization

Granulation

Pressing

Technology elaborated for brown mud utilization

Raw material: brown mud

Additives: bauxite clay, mining refuse, sandstone

Storage

Measuring

Grinding

Homogenization

Granulation

Pressing

The comparison of technical data of glazed wall tiles is shown as follows:

The comparison of economic efficiency of production is shown as follows:

b. Results of manufacturing of bricks from brown mud and fly-ash on pilot/demonstration scale:

By pre-treatment of the coal at the plant power station before burning, based on a process, patented by the author, a fly-ash with acquired hydraulic bonding properties may be produced. A sample of this pre-treated fly-ash was tested as the second main component of a mixture - see initial composition data below.

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* L.O.I. - 8,35 ζ ; C - org - 0,42 ζ

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The ratio of 60 % brown mud and 40 % pre-treated fly-ash was used $\omega_{\rm{eff}}$ with the application of a new technological scheme as follows:

Clay mining

Drying of brown mud by hot flue gas from rotary kiln

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Storage

Storage

Table 3: Composition of brown aud and fly-ash

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Firing in Hoffmann-kiln (10-90 days) Delivery of the bricks from the 5th day

Discharging the bricks from the kiln intermittently after cooling

Delivery on the 30th-120th day after shaping

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The comparison of technical data of the bricks is shown as follows:

Comparison of economic efficiency of production (Data related to a production unit of 10 million pcs/year)

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Payback period of the investment 10,4 year 2,0 years

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7. Conclusions:

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The processing of bauxite to aluaina leads to the accumulation of solid residues in large quantities. The handling and disposal of this material is expensive and poses continuous environmental problems and difficulties. Therefore, many countries are looking for ways and means of decreasing this environaental hazard through profitable utilization of these residues on a large scale. Unfortunately, the progress made towards identification of technically and economomically viable technologie; in processing red mud on a sufficiently large industrial scale bas been extremely slow until now.

A new process utilizing red mud has been developed by the author with the production of floor and roof tiles, bricks and light construction blocks containing $40 - 90$ \bar{x} of red mud and other common additives usually locally available. Recongnizing this industrial opportunity, some developing countries have requested through UNIDO to study their specific cases and projects have been implemented for Jamica, India and China. These projects prepared techno-economic assessments of industrial processing of red^{*} mud from alumina production and included laboratory and pilot scale elaborations and testings of mixtures from red mud and other wastes with local additives.

In the case of Jamaica the tests yielded successful technical results and it is now proposed to apply these results for additional elaboration of energy saving technological variants. In the case of China, the study of bauxite residues from the Shandong alumina plant showed that the brown mud available there can also economically be processed into value added building materials. The report recommended ¹the establishment of a plant that could produce 100 million bricks and 2 million n^2 tiles per year.

In case of India, the puting up of industrial processing for sludges from the steel industry is in progress and based on the study results industrial units, based on cold techology are proposed to be set up for red mud and garnet sand residues.

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