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Case studies for the valorisation of Bayer's process bauxite residue: aggregates, ceramics, glass-ceramics, cement and catalysis

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Abstract

A variety of uses for Bayer's process bauxite residue has been investigated the previous years in a collaborative scheme between Aluminium of Greece and a number of institutions. Efforts have been primarily directed for the production of high-volume building materials, i.e. aggregates, ceramics, cement, although other, higher added-value applications have been also investigated, i.e. glass-ceramics and catalysis. In this work, a brief overview is presented.

Introduction

Aiming to apply industrial ecology practices and potentially create a cluster of collaborating companies, setting up an "industrial symbiosis" example, a project was proposed in 2002 concerning the utilisation of Bayer's process bauxite residue, BR (*i.e.* red mud). The project envisaged collaboration between Aluminium of Greece S.A., as the supplier of BR, one heavy clay ceramics' company, Panagiotopoulos S.A., as well as the two major cement companies in Greece, Heracles General Cement Company S.A. and Titan Cement Company S.A., as the end-users. The laboratory of Materials and Metallurgy, dept. Chemical Engineering, University of Patras would serve as the research responsible unit.

The project resulted in the successful installation of a high-pressure filter-press and a new product to the market under the name Ferro-alumina, FA. Results on the use of FA in laboratory and pilot-plant scale were promising and FA has been used industrially. Eventually, the investigated paths for FA utilisation exceeded the original vision and in conjunction with work conducted at other Greek universities, a substantial amount of research work has been generated. This work will try to shed some light into selected case studies.

Aggregates

Lightweight aggregates exhibit good thermal and acoustic insulation, as well as, fire resistance properties and constitute a major component in lightweight structural concretes (see also contribution by Chris Cheeseman in this Symposium Book). In the work by Anagnostopoulos *et al.*¹, synthetic lightweight aggregates were produced by combining fly ash and bottom ash from lignite's combustion with FA and a small amount of metallurgical grade limestone. The mixture design was based on a steady content of bottom ash, at 60 wt%, as the carbon content of this material was also the fuel of the process. Fly ash varied between 7 and 32 wt%, whereas FA varied between 5 and 30 wt%. Metallurgical grade limestone at 3 wt% was also added to facilitate the formation of the pellets. The compositions are presented in Table 1.

Table 1: Compositions of the mixtures for the aggregates

Mixture symbol	Bottom ash (wt%)	FA (wt%)	Fly ash (wt%)	Metallurgical lime (wt%)
M1	60	5	32	3
M2	60	10	27	3
M3	60	15	22	3
M4	60	20	17	3
M5	60	25	12	3
M6	60	30	7	3

The process involved two steps: granulations and grate sintering. Granules of 3-10 mm were formed in a granulating rotating disc, working at a slope of 45°, by adding the minimum required amount of water to the mixture. Sintering takes place in a "sinter-pot". The process is started with the ignition of a coal layer placed at the surface of the bed. Air is drawn downwards through the grate, by means of an exhaust blower connected underneath to the grate. In this way, suction pressure is created through the bed. The combustion zone developed initially at the top layer travels through the bed raising the temperature of the bed layer by layer. The firing cycle lasts for a few seconds and results in a hardened porous "cake", comprised of porous aggregates. The sintering temperature, measured by thermocouples, is approximately 1250°C. The resulting aggregates were tested for porosity, water absorption and bulk density, according to ASTM C373–88, and unit weight, according to ASTM C29, whereas the crystalline phases were identified by XRD. Concrete specimens with aggregates were also prepared and tested, according to EN196-1 specifications. The photograph of the sinter pot with the porous cake is depicted in Figure 1. Results for the aggregates and the concrete specimens are presented in Tables 2 and 3.

Table 2: Open porosity bulk and density of the produced aggregates

FA, %	Open porosity, %	Bulk density, g/cm ³
5	60.83	1.02
10	52.93	1.12
15	43.86	1.23
20	37.55	1.38
25	35.05	1.42
30	21.64	1.8

Table 3: Over dry density of the final concretes samples with aggregates and the corresponding compressive strength after 1, 7 and 28 days

Mixture	Oven dry concrete density, kg/m ³	Compressive strength, 1d (MPa)	Compressive strength, 7d (MPa)	Compressive strength, 28d (MPa)
M1	1570	8.6	24.6	34.4
M2	1660	9.3	30.7	38.1
M3	1670	9.0	29.2	38.9
M4	1710	9.3	27.7	37.9
M5	1750	8.3	27.2	35.5
M6	1790	7.5	28.3	33.9



Figure 1: Sinter pot open after firing; the porous cake appears in the center

The major conclusions can be summarised as follows: a) increase in FA addition in the sintering mixture results in increase of the unit weight and density of the produced aggregates; b) porosity and water absorption values of aggregates vary between 35–61% and 21–61% respectively, and bulk density values vary between 1.02 g/cm³ and 1.80 g/cm³, aggregates produced with FA addition up to 20 wt% are characterised as lightweight ones, according to ASTM 330 specifications; c) the compressive strength of concrete made with the produced aggregates shows that addition of FA up to 15 wt% in sintering mixtures enhances the strength; d) addition of FA between 20 wt% and 30 wt% results in decrease of concrete strength, as well as, in further increase of the concrete density; e) FA in combination with bottom ash and fly ash can be considered as a potential raw material for the production of LWA by means of the proposed sintering process.

Ceramics

A wide range of ceramics was produced with FA amount ranging from 10 to 100 wt% in the body mixture. The interested reader can retrieve more information in the respective published work.²⁻⁸ The most promising route according to the authors' experience has been summarised in an invention.⁹

In general, the use of FA in ceramic production is technically feasible. However, the benefits are case specific per plant. FA will provide red colouration and can substitute part of the raw materials. On the other hand, it is doubtful that the quality of the end-products will be improved if no action is taken. Moreover, in many cases, ceramic producers have secured reserves of low-cost raw materials within their vicinity or produce red products already. Therefore the use of FA is not straightforward. A more holistic view, if needed imposed by legislation, on the sustainability of current industrial practices and use of virgin raw materials would probably promote the use of FA.

The major drivers for the use of FA in the ceramic industry are: a) reduction in energy required for milling of the raw materials as FA is fine, b) substitution of virgin raw materials and c) red colouration. The major barriers are: a) availability of other low-cost raw materials in the vicinity of the plants, b) transportation cost, c) requirement of a silo to store FA and avoid air borne or water transferred particles as well as any leaching, d) no observed improvement of quality of end-products if no actions are taken, e) opportunities for better end-products with FA will necessitate changes in production process and ceramic industry is very reluctant to proceed in this direction, f) strong market barrier imposed by higher levels on natural occurring radioactive elements compared to clay minerals, g) strong perception barrier as FA is still tagged as a "waste".

Glass-ceramics

Glass-ceramics are polycrystalline materials of fine microstructure that are produced by the controlled crystallisation (devitrification) of a glass.¹⁰ Known examples of waste-based glass-ceramics are “Slagsital”¹¹ and “Slagceram”¹² whereas the main applications are in the building industry (as floor and roof tiles or road surfacing panels). In the work by Bernardo *et al.*¹³ a glass frit was obtained by melting a mixture of FA, fly ash from lignite combustion, residues from the polishing of porcelain stoneware tiles and CaO. The glass-frit was subsequently pressed and sintered. This process is also known as “sinter-crystallisation” and is based on the viscous flow sintering of glass frits with concurrent crystallisation.

The different components were mixed in the weight proportion FA/fly ash/polishing wastes/CaCO₃ = 10/29/40/21. The mixture was converted into a glass at 1400°C for 2 h. After quenching, two kinds of powders having a maximum dimension of 37 and 75 µm were studied. The firing behaviour was evaluated by dilatometry (on a glass rod) and DTA/TGA (for the powders). The final samples were made by uniaxial pressing of the fine powder and sintering by using two different heating cycles. The “conventional” sintering, involves heating rate of 10°C/min, soaking time of 0–3 h, up to 900°C. The “rapid” sintering involves sintering directly at 900°C, and soaking time of 0.5–1 h. For the sintered glass-ceramics, the following properties were measured: bulk and true density, four-point bending strength, Young’s modulus, micro-hardness and resistance to chemical attack. Microstructure was analysed by SEM and XRD. The major results are presented in Table 4.

The key findings of the investigation may be summarised as follows: a) FA, fly ash and ceramic tile polishing wastes may be converted, by proper mixing, into a glass prone to surface crystallisation, leading to multiphase glass–ceramics; b) the fast surface crystallisation is reasonably associated to the oxidation state of iron ions, which also promotes the development of a not frequently encountered pyroxene (esseneite) as one of the main crystal phases; c) the enhanced nucleation activity of fine glass powders allows short thermal treatments; in particular, dense and well crystallised glass–ceramics may be obtained even with a “rapid sintering” treatment, promising for the manufacturing of glass–ceramics with the well known, simple and economic processing of traditional ceramic tiles; d) the substantial crystallisation led to remarkable mechanical properties; bending strength and Vickers micro-hardness exceed 100 MPa and 7 GPa respectively; e) preliminary chemical tests on glass–ceramics indicate a promising chemical durability.

Table 4: Physical and mechanical properties of the investigated sintered glass–ceramics

Sintering temperature (°C)	Soaking time (h)	Heating mode	Bulk density (g/cm ³)	Closed porosity (vol%)	Elastic modulus (GPa)	Bending strength (MPa)	HV (GPa)
900	0.5	C	2.82 ± 0.01	4.2	99.4 ± 1.2	89.6 ± 22.6	
900	1	C	2.84 ± 0.02	4.9	99.9 ± 0.7	100.9 ± 14.4	
900	2	C	2.84 ± 0.01	4.4	125.8 ± 4.6	132.6 ± 16.5	7.3 ± 0.3
900	0.5	R	2.80 ± 0.02	5.6	97.2 ± 7.0	96.5 ± 15.7	
900	1	R	2.82 ± 0.01	3.8	103.2 ± 6.9	102.9 ± 20.5	7.0 ± 0.3

C: conventional, R: rapid

Cement

Two different routes, resulting in two types of clinkers with FA, have been investigated: Ordinary Portland Cement (OPC) and belite-rich. Part of the results can be found elsewhere;^{14,15} all the work presented herein is included in the PhD thesis of I. Vangelatos.¹⁶ The first route focused on the introduction of FA as a raw material in the meal for OPC clinker production.¹⁴ This approach was the pragmatic one, taking into account that industries in Greece, and also worldwide, produce typically OPC quality clinker. The second route was concerned with the introduction of FA as a raw material for belite-rich clinker production.¹⁵ Actions were also taken in order to address the low early strength, typical for belite-rich clinkers. This was the visionary approach: although high-belite clinker is produced only at a very small scale it does offer comparable advantages and could be potentially the future standard product for the cement industries.

OPC production with red mud

For the preparation of the OPC raw meals 1, 3 and 5 wt% of FA was incorporated in a mixture of limestone and sandstone. The corresponding percentages of the materials were adjusted in order to keep the LSF index similar to that of the reference mixture and the alumina (AM) and silica (SM) modulus within the limits required for OPC production. The reference mixture was delivered by Titan Cement Company S.A. The composition of the meals was (in wt%) limestone/sandstone/ferroalumina: 87.75/11.25/1.00, 86.50/10.50/3.00 and 85.30/9.70/5.00.

For the clinker production, the meals were initially mixed with a minimal amount of water and shaped into spheres, were heated subsequently at 1000°C for 4 h and finally were fired at the designated temperature based on the burnability tests (ranging between 1450 and 1550°C, soaking time 40 minutes). Their mineralogical

composition was derived applying Bogue's equations. Cement was produced by mixing and co-grinding the clinker produced above with 5 wt% gypsum. The specific surface of the so-produced cement was measured with a Blaine apparatus according to EN 196-6. Mineralogical composition of the samples was determined by XRD analysis. The setting time and the water requirement were determined by a Vicat needle apparatus and a Vicat probe, respectively, according to EN 196-3. Compressive strength of 40x40x160 mm³ mortar prisms at 2, 7, 28, 90, 180 and 360 days, was determined according to EN 196-1. The results are presented in Table 5 and 6.

Table 5: Physical properties of the produced cements

Physical properties	Blank	1 wt% FA	3 wt% FA	5 wt% FA
Specific Surface (cm ² /g)	3730	3810	4010	3870
Initial Setting Time (min)	100	100	80	90
Final Setting Time (min)	160	140	160	150
Water Demand (wt%)	21.6	22.4	22.6	22.2

Table 6: Compressive strength of the produced cements and comparison with CEM I. NR: not required

Days	CEM I		Blank	1 wt% FA	3 wt% FA	5 wt% FA
	42.5N	52.5 N				
2	≥ 10.0	≥ 20.0	19.2	26.5	27.4	30.8
7	NR	NR	39.2	48.2	42.9	44.3
28	≥ 42.5	≥ 52.5	55.6	62.9	57.5	58.4
90	NR	NR	57.5	69.6	65.2	63.0
180			60.2	71.2	67.8	68.3
360			64.3	73.1	69.8	70.2

The conclusions of this work are summarised as follows: a) the addition of FA as a raw material in the meal for OPC production is feasible up to the 5 wt%, with typical range 2-3 wt%, depending also on the chemical composition of the other raw materials, b) FA addition does not affect the thermal behaviour of the meals and typically free lime less than 1 wt% can be obtained for firing temperature of 1450°C; c) the microstructure of clinkers with FA is comparable to the reference sample; d) characterisation of the cements showed that differences in surface area, water requirement and setting time are negligible, e) compressive strength after 2 days curing is over 20 MPa, whereas after 28 days, it varies from 55 to 63 MPa. These values rank the obtained FA cements in CEMI 52.5N category.

Belite-rich clinker

The raw materials used for the preparation of the mixtures were industrial grade limestone, high-purity industrial grade limestone (HPL), FA, shale, bauxite and gypsum. Three clinkers were designed, based on modified Bogue's equations. The goal for the first blend was to achieve high-belite content, > 70 wt%, in conjunction with C_4AF content > 12 wt%, which is the limit for OPC. This would result in higher utilisation of FA compared to addition for OPC production where the levels of FA usually range at 2–3 wt%. The other two blends aimed at the formation of C_4AF with concurrent development of sulphur-bearing hydraulic compounds, in order to enhance the early strength development. The above resulted to a decrease of C_2S level at 40–50 wt%. The compositions (in wt%) for calcite/HPC/FA/shale/bauxite/gypsum are as follows: BC: 82.80/0/4.20/13.00/0/0, BSFC1: 70.00/0/2.00/0/12.00/16.00, BSFC2: 38.00/14.20/8.00/0/19.00/20.80. The production of the cements took place in a similar way as described above for OPC type cements. In Table 7, the physical properties of the resulting cements are presented, as well as, the compressive strength of the cements for 1, 2, 7 and 28 days.

Table 7: Physical and mechanical properties of the cements

	BC	BSFC1	BSFC2
Specific surface (cm^2/g)	4100	4850	4430
Initial setting time (min)	140	25	<1
Final setting time (min)	200	35	<1
Water demand (wt%)	21.5	28.7	n.d.
Day	Strength (MPa)		
1	-	17.6	14.9
2	5.0	25.8	23.5
7	17.5	36.8	30.1
28	53.7	43.7	34.2

n.d.: not determined

The conclusions of this work can be summarised as follows: a) the main phases present for BC are C_2S and C_4AF . The phases C_3A and C_3S are also present at a smaller extent. For BSFC1 and BSFC2, the identified mineralogical phases are C_2S , C_4AF , $C\hat{S}$, as well as $C_4A_3\hat{S}$ (Klein compound or Yeelimite). The formation of these phases is in line with the original design of the blends; b) the physical properties of the belite-rich cements, such as setting time and water demand, correspond to their mineralogical assemblage. In particular, BC has long setting time and workability, whereas the cements with the sulphur compounds set faster, as a result of the hydration reaction of Klein's compound and gypsum; c) the reference BC cement has a compressive strength of only 5 MPa after 2 days, as expected due to the high belite and low alite

content. For 28 days, the strength of BC is satisfactory, reaching 53.7 MPa. The early strengths in the belite-sulfoferrite cements are considerably improved, compressive strength after 1 day is 17.6 and 15 MPa and rises to 26 MPa and 23.5 MPa the next day, for BSFC1 and BSFC2 respectively. Nonetheless, the long term strength of 28 days is reduced compared to BC. The strength for BSFC1 is 43.7 MPa whereas for BSFC2 is 34.2 MPa.

Catalysis

In the present study the feasibility of the use of FA as catalyst for the growth of carbon nanotubes was examined.¹⁷ Significant interest in the formation of carbon nanomaterials, and especially carbon nanotubes (CNT's), was promoted by the observation of Iijima¹⁸ in 1991 according to which filamentous carbon (produced during the evaporation of carbon electrodes using the arc-discharge method) had a nanometer size tube structure. Since then, CNT's have drawn much attention for many potential applications, which derive from their unique electronic and mechanical properties.^{19,20} The realisation of this idea can promote the valorisation of FA and in addition will decrease the production cost of carbon nanotubes, thus making the implementation of CNT's in various applications economically viable. It should be emphasised that this is the first time FA was employed as catalyst for the production of CNT's.

Five different qualities of FA have been prepared as catalysts for the carbon deposition experiments. FAI corresponds to the FA material "as-is". FAII derives after grinding the material in order to reduce the mean particle size and increase the specific surface area. FAIII derives after sieving at particle sizes < 90 µm. The goal of this step is the enrichment of the FA in sodalite,² and the increase of the specific surface area of the material, both of which can assist the catalytic growth of CNT's. FAIV derives after chemical treatment as described elsewhere.²¹ This procedure can also increase the specific surface area of the FA. Finally, FAV derives from chemical and subsequent thermal treatment of the original FA, to achieve an even greater increase of the specific surface area of the final material.

Catalysts were characterised by XRD and BET. The deposition experiments took place in a CVD reactor. The deposition experiments were conducted at 700 and 800°C. Helium flow was used for purging the chamber and during the heating of the catalyst. After temperature stabilisation, ethylene was introduced into the reactor, at 30% concentration in helium. Upon completion of the deposition experiments, the final products were analyzed with Scanning Electron Microscopy (SEM) and Raman

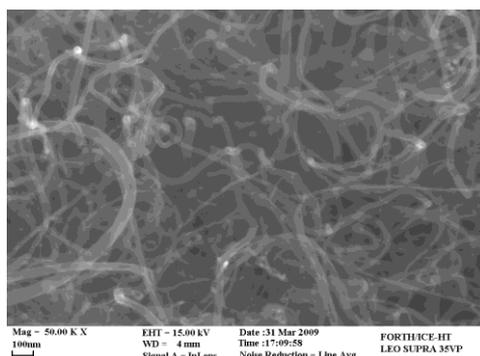


Figure 2: SEM micrographs of carbon nanotubes produced by ethylene decomposition at 700°C over FA3.

spectroscopy. Raman spectra were excited by a linearly polarised monochromatic radiation at 785 nm (red line). Table 8 provides an overview on some of the results whereas CNT's are depicted in Figure 2.

Table 8: Specific surface areas, initial growth rates and yields of various FA qualities for CNT's deposition at 700°C with 30% C₂H₄ in He

FA qualities	BET Specific surface area (m ² /g)	Initial growth rates (mg/s)	% Yield over catalyst
FA1	10	4.33	225
FA2	15	3.34	167
FA3	8	7.40	323
FA5	40	9.30	488

The conclusions of this work were: a) The optimum temperature for attaining high yield of CNT's synthesis was determined to be 700°C, b) The chemically and thermally treated FA, having the higher specific surface, was found to be the best one for producing high purity multi wall carbon nanotubes (MWCNT's), c) the presence of SWCNT's was ascertained by the existence of RBM Raman peaks in some of the tested FA qualities.

Other uses

The work presented above covers mostly the collaboration between University of Patras, Greece and Aluminium of Greece S.A.. Other uses of bauxite residue have been studied elsewhere in Greece and a brief, non-exhaustive, overview is given as follows: a) as revegetation cover,²² b) as filling material in mine open pits,²³ c) in geotechnical application, such as road embankment,²⁴ d) aimed for use in iron ore industry after reductive roasting and magnetic separation,²⁵ e) for recovery of trace and minor elements,^{26,27} f) for production of alkali-activated construction materials.²⁸

Conclusions

A variety of uses for Bayer's process bauxite residue have been briefly reviewed. The ones with already industrial application in Greece concern the production of heavy clay ceramics such as roofing tiles and bricks and OPC cement. Other potential uses are the production of aggregates and belite-rich, low energy demanding cements. Applications with higher added value have been also presented, *i.e.* glass-ceramics and catalysis.

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