# TWO STAGE BAUXITE RESIDUE UTILISATION METHOD

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## Abstract

*There is estimated deposit of 1 Mt of red mud from $Al_2O_3$ production by Bayer process and 9 Mt of brown mud from $Al_2O_3$ production by sinter process in Slovakia. Despite of many years of research, there was no success in its utilisation. To solve this problem, we have created cooperation between scientific and educational institution and industrial production enterprises. We proposed two-stage red mud utilisation method by metallurgy process. This method was directly applied in the cast iron production, 2 Kt of grey cast iron was produced with the addition of aggregated bauxite residue. Properties of the produced grey cast iron and chemical changes after addition of bauxite residues, as well as influence on cupola furnace lining are favourable. The method has potential to succeed on a full-scale basis.*

## Introduction

The aluminium-based materials have been the most important ones during the recent decades. Production of aluminium in the world represents a huge amount of bauxite mining and electricity consumption. This production is associated with production of bauxite residue up to 2.5 tonnes per tonne of alumina produces, typically between 0.7 and 2.0 tonnes.[1] Bauxite residue is one of the largest by-products in the world. The global inventory of bauxite residue reached an estimated 2.7 billion tonnes in 2007 increasing at 120 million tonnes per annum.[2] In spite of that over 50 years of research, hundreds of patents, no significant utilisation is realised.[3] Production $Al_2O_3$ and Al in Slovakia began gradually since 1959. Since that time bauxite residue has began to accumulate on waste dumps. It has reached an area of almost 45 ha, height 45 m, circumference 3 km. There is estimated deposit of ca 1 milion tonnes of red mud from $Al_2O_3$ production by Bayer process and 9 milion tonnes of brown mud from $Al_2O_3$ production by sinter process. Despite of many years of research, there was no success in its utilisation. Several years of successful germanium production with bauxite residue utilisation did not significantly affect the deposited amounts of bauxite residues. Now was dumping place closed and recultivated. The aim of this paper is to show so far not examined possibility of using bauxite residue in the production of grey cast iron. We proposed the two-stage method for processing bauxite residue by metallurgical method and its verification. We used this method directly in the production of cast iron.

## Cooperation between scientific and educational institution and industrial production enterprises to facilitate research of new technology on base bauxite residue

The basic research of the use of bauxite residue was realised in 2000.[4] Later based on the implementation of basic knowledge in practice we have created cooperation between scientific and educational institution and industrial production enterprises to facilitate research of new technology on base bauxite residue (Figure 1). The possibility of using bauxite residue in the production of cast iron have been verified in practice with the company 1 (Foundry) on the basis of this cooperation in the long term. Within the research, we ensured cooperation with the company 2 for compacting bauxite residue. In the next step we created collaboration with the company 3, which treated waste debris from cast iron production.

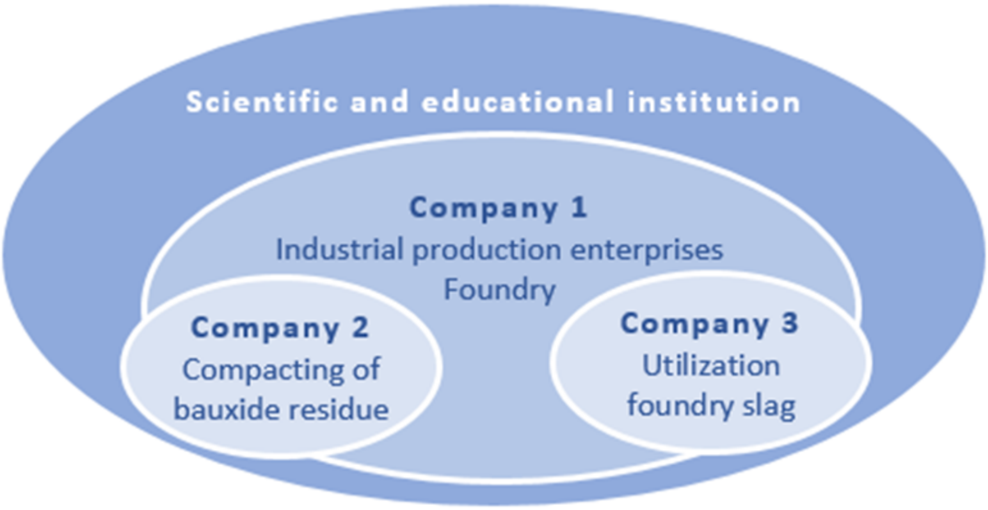


**Figure 1:** The involvement of the research university in applied research with individual companies from practice

## Two-stage bauxite residue utilisation method in the cast iron production

It has so far been examined many potential possibilities of processing bauxite residue.[5] Consequently, most of these techniques are uneconomical and not used commercially. Aluminium producer ALCOA has a process to carbonate red mud using

$CO_2$ from industrial gas streams. The resulting "red sand" is used to make cement and in road construction. Others have developed processes to recover iron and rare-earth metals from red mud. But so far, only 2 million metric tonnes of red mud is being repurposed annually-less than 2 % of the amount being generated.[6] Orbite Process for treating red mud with HCl was found according to the patent of the authors Bodreault (2013)[7] for obtaining Al, Fe, Ni, Co, Mg, rare earth elements, rare metals, etc. and various other components such as $TiO_2$, $SiO_2$ etc. Interesting is processing of red mud from alumina production in the smelting unit MAGMA reaching high temperatures from 1650 up to 1900 °C.[8] Specific consumption of energy carriers for processing of 1 tonne of red mud: thermal coal up to 200 kg; natural gas up to 50 $m_n^3$; technical oxygen up to 100 $m_n^3$. Great potential possibilities of utilisation of bauxite residue are for pig and cast iron smelting and steel manufacture, especially arc furnace systems.[9-11] But yet there were no information on use of bauxite residue for the production of cast iron in the cupola furnace. Only the earlier US patent 2750279 A, described the reaction products of hydrogen fluoride with iron compounds in general, and in particular with siderite, hematite, limonite, magnetite, scrap iron, forging scale and red mud, the reaction product of hydrogen fluoride with siderite being preferred.[12] Those processes were not realised. We proposed and in the real form performed two-stage bauxite residue utilisation method in the cast iron production (Figure 2).

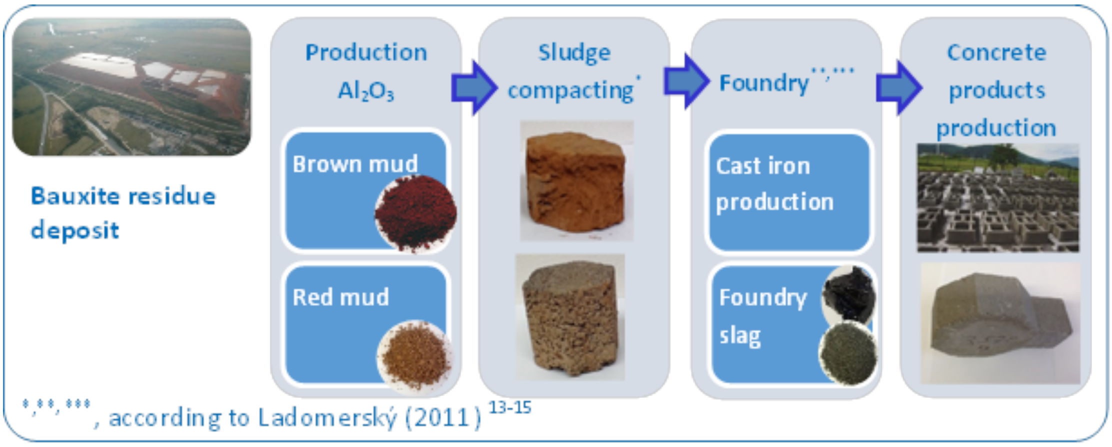


**Figure 2:** Simplified two-stage bauxite residue utilisation method

As basic material for metallurgical test samples were compacted bauxite residue according to the patent Ladomerský et al. (2011a),[13] which were, along with other essential raw materials needed for the production of cast iron, we place into the cupola furnace according to a predetermined scheduled tests. Metallurgical process follows the current technological process. The tests were performed in a foundry, which comprises two hot air cupolas with the continuous metal removal. The average melting output of the cupola is 7.8 $t.h^{-1}$, metal temperature in the siphoning is 1480 °C. 25 kg of limestone is dosed for the classical melting of 1000 kg of the batch. For these operating conditions have gradually reduced the proportion of limestone and increased bauxite residue.

## Results in full scale factory production with the addition of aggregated bauxite residue

### Influence on cupola furnace lining

In addition to our knowledge only in Romania is known the using of bauxite residue in steel production to reduce the ilmenite consumption needed for protection of the hearth refractories against erosion.[1] In our experiments in full scale factory grey iron production the addition was made in the amount of 1.5 to 17 kg of the bauxite residue per tonne of the cupola charge. We have achieved partial replacement of limestone (the most for dosing 10 kg limestone and 17 kg bauxite residue for 1000 kg of the batch) and reduction of abrasion of cupola furnace's refractory clay. The greatest achieved reduction of the lining wear was 65 %.

### Chemical changes

Chemical and mineralogical composition and granulometric composition bauxite residues varies depending on the location and depth of the collection pond and saving time. This predetermines how to use them.[16] Operating experiments we conducted with bauxite residues containing the elements in the Table 1.[17] After application of bauxite residue in the cupola there was an increase of Al in the melted cast iron up to 25 %. There was a decrease of the iron loss of Si (Si content higher in metal and lower spread suggests better use of FeSi75 for melting and its lower iron loss) and the long trial mode of production of cast iron with application of bauxite residue achieved savings of FeSi75 of about 15 to 26.5 %.

For the samples we further evaluated foundry slag size distribution and elemental analysis by the ED XRF method. Foundry slag size distribution depends practically only on the applied technology and practically does not depend on the addition of bauxite residues. Elemental analysis of foundry slag in the majority of the elements found highly significant differences among the ruins of the standard production and foundry slag from the production of grey cast iron where bauxite residue was applied. The most significant change was a decrease in the concentration of Fe by 36 % and Mn increase by 15 %, Si by 10 % in the foundry slag from the production of grey cast iron with the addition of bauxite residue. Low concentrations of Zn and S also decreased significantly.

**Table 1:** The content of selected elements determined using the ED XRF method in brown and red mud from Žiar nad Hronom (Slovakia)[17]

| | Red mud [ppm] | $U_n$ [%] | Brown mud [ppm] | $U_n$ [%] |
|---|---|---|---|---|
| Al | 46900 | ±10 | 36500 | ±10 |
| As | 84.8 | ±20 | 96.4 | ±20 |
| Ca | 161522 | ±15 | 121000 | ±15 |
| Cd | 1,20 | ±40 | 0,300 | ±40 |
| Cl | 522 | ±40% | 316 | ±40 |
| Cr | 312 | ±30% | 269 | ±30 |
| Cu | 120 | ±30% | 48.6 | ±30 |
| Fe | 158000 | ±10% | 183000 | ±10 |
| Ga | 18.0 | ±40% | 14.5 | ±40 |
| K | 1530 | ±15% | 956 | ±15 |
| La | 213 | ±30% | 171 | ±30 |
| Mg | <5000 | - | <5000 | - |
| Mn | 1920 | ±25% | 728 | ±25 |
| Na | <15000 | - | <15000 | - |
| Ni | 387 | ±30% | 297 | ±30 |
| P | 1280 | ±40% | 377 | ±40 |
| Pb | 97.3 | ±25% | 106 | ±25 |
| S | <10.0 | - | <10.0 | - |
| Si | 57400 | ±10% | 35900 | ±10 |
| Sr | 675 | ±10% | 306 | ±10% |
| Th | 45.9 | ±10% | 55.3 | ±10% |
| Ti | 20800 | ±30% | 12200 | ±30% |
| V | 454 | ±40% | 328 | ±40% |
| Y | 250 | ±10% | 94.4 | ±10% |
| Zn | 201 | ±15% | 66.2 | ±15% |

## Properties of the produced grey cast iron

During each experiment of the model melt (after the addition of bauxite residue into the cupola furnace), we investigated the microstructure and the mechanical properties of individual melts. The microstructure of samples for metallographic observation after etching by 2 % NITAL were compared with STN 42 0461.[18] The mechanical properties of cast iron were determined according to the following standards: STN 42 22420;[19] STN 42 2306;[20] STN 42 2307; [21] STN 42 2304; [22] DIN GGG 403;[23] EN 1563: EN GJS 400.LT.[24] These properties are observed even during normal melting, i.e. without bauxite residue additives. The addition of bauxite residue to the cupola furnace influences the microstructure of the cast metal, especially the graphitisation occurring in cast irons during cooling of molten metal. The amount of formed graphite, the form in which it is present, and its degree of distribution, as well as the free carbon dispersed throughout the solid solution when the iron is cooled, all have a substantial effect on the physical properties of the iron casting obtained. Adding of bauxite residue into the metallurgical process of cast iron production favourably influenced their microstructure. The addition of bauxite residue resulted in a larger share of an appropriate fine-grained pearlite structure and finer shape and distribution of the lamellar and spidery graphite G 23. In terms of size graphite there were found slight improvements and a shift to finer graphite, the ferrite content remains unchanged. This influence of the structure is due to increased surface hardness, increased strength and improved impact strength of the castings made with the application of bauxite residue. The application of bauxite residue into to the cupola furnace significantly increased surface hardness of grey cast iron castings by about 10 to 70 %, the strength by 5 to 25 % and a lining toughness by about 5 to 15 %. Differences of other characteristics were statistically insignificant.

## Conclusions

The paper reports the results of the pilot project utilising bauxite residue in the manufacture of grey cast iron. The new two-stage process for bauxite residue metallurgical processing method and verified directly in production was proposed. The possibility of use of bauxite residue in the production of grey cast iron was actually confirmed. Long-term full scale production experiments proved the feasibility of two-stage bauxite residues utilisation method in terms of cost effectiveness, potential adverse effects and other effects. Applying the sludge into the metallurgical process of the cast iron in the cupola furnace may for example partially replace expensive ferroalloy, which are added to the metallurgical process of the cast iron production. We have achieved partial replacement of limestone (max. 10 kg limestone and 17 kg bauxite residue for 1000 kg of the batch) and reduction of abrasion of cupola furnace's refractory clay up to 65 %. Properties of the produced grey cast iron and chemical changes after addition of bauxite residues, as well as influence on cupola furnace lining are favourable. Two-stage bauxite residues utilisation method has potential to succeed on a full-scale basis.

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21. STN 42 2307 Pearlitic spheroidal graphite cast iron 42 2307.
22. STN 42 2304 Ferritic spheroidal graphite cast iron 42 2304.
23. DIN GGG 403 ductile cast iron grade.
24. EN 1563: EN GJS 400.LT Grade ductile iron.