ASH UTILIZATION WITH SILICA AND METALS RECOVERY

Sol Shcherban
The International Association of Sciences, Inc., 110 Bennett Ave., # 3H
New York, NY 10033

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ABSTRACT

The annual generation of electric power in the United States results in production of over 43 million tons of fly ash. Only about 22% of this amount is presently utilized. Neither of the used ash applications requires the recovery of metals and other valuable components (i). In the process of studying, there is another group of methods based on direct recovery of metals from ash (ii). This paper continues presentation of new technologies for ash processing with silica pre-extraction process (SP-process) and recovery of metals. Silica in ash represent about 40-65% of the total, therefore the possibility of silica recovering and converting into a wide variety of pure chemical silicate products with the predetermined properties is one of the main advantages of new technologies. For technical and economic features these perspective technologies present the third new group of methods of ash utilization (iii).

INTRODUCTION

In 1993, approximately 43.4 million metric tons of coal combustion fly ash were produced by the electric utilities in the United States [1]. Only about 22% of this amount was used mainly for cement, concrete products, and other [2]. For these applications, ash is used in an unsophisticated way without recovery of same components (i). The low level of ash utilization shows that such applications are insufficient for the complete utilization of fly ash, which is why there is a constant need for finding new ways to increase utilization of fly ash. For a significant increase in ash utilization, it is necessary to expand the assortment of useful products which can be produced from ash.

Aluminum is one of the major ash components. Many chemo-metallurgical methods were proposed for recovery of alumina from high-silica alumina-containing ores and industrial by-products including ashes (ii). As applied to ashes, these methods have two fundamentally important deficiencies which make them non- or low- profitable. One of them consists of great outlet streams of raw materials and intermediate products which leads to high capital and operating costs of alumina production [3-5]. As it will be shown below, no less important is the second deficiency - withdrawal of silica from the technological process in the form of solid residue. Conversion of silica into solid residue restricts the possibility of its utilization while silica represents the largest component of ash (40-65% of the total).

This paper continues to present new technologies for ash processing which makes it possible to reduce the outlet streams of raw materials and intermediate products, and to put out the most part of silica in the form of chemical silicate products (iii). The earlier papers described the background and main operations of new technologies [6,7]. The purpose of this paper is to expose main features of new technologies with silica pre-extraction process and to evaluate their possible influence on the economic showings.

EXPERIMENTAL

Object of research.
It is important to distinguish the varieties of ashes for choosing methods of the metal recovery, depending on chemical and mineralogical compositions of ash. As object of present consideration, ashes with low content of calcium and magnesium compounds were chosen. Ashes of some typical United States' coals of West Virginia, Ohio, and Illinois as well as ashes of Ekibastuz (Kazakhstan, Russia), Donetzk, Kuznetzk, Podmoscow (Ukraine and Russia) coals are suitable for this consideration. The chemical analysis of ashes and traditional raw materials used by aluminum industry are given in Table 1.

Prospects for ash using for alumina production. Strategy.
There are serious reasons to be doubtful about prospects of ashes to compete with traditional aluminum raw materials if ash is used as a monomineral material like bauxite for aluminum production only. The comparatively low content of alumina, high content of silica, and presence of aluminum mainly in the form of chemically stable mullite [6,7] result in great outlet streams of materials which have to be processed by the most power-consuming operations as roasting, sintering, and other (Table 2). Finally, this leads to the high capital and operating costs of alumina production from ash [3-5].

However, available industrial experience of alumina production shows that high silica materials can be processed profitably if they are used as polymineral raw materials for production of alumina and salable by-products as soda, potash and alkali for nephelines or sulfates for alunites. But ashes do not contain any considerable quantities of alkali (Table 1) whose availability creates a profitable technology of nephelines processing. Therefore, silica- the largest component of ash, can be used as a salable by- product for ashes. The foregoing shows:

-ash can not be processed profitably as a monomineral raw material used for aluminum production only

-to make aluminum production competitive, it is necessary to utilize silica that represents the largest component of the ash

-it is important to develop less power-consuming technologies by means of lowering outlet streams of raw materials and intermediate products.

Methods of ash utilization
Taking into account the principal importance of silica utilization, it is useful to examine all of the methods from the viewpoint of silica recovery and utilization. From this standpoint, all of the methods can be subdivided into three groups (Figure 1):

(i) Ash uses without recovery of components from ash (cement, concrete products, road base and subbase, structural fills, embankments, filler, grouting, waste stabilization and other)[2].
(ii) Direct metallurgical processing of ash for alumina (aluminum) production without recovery of silica.
(iii) Ash processing with silica recovery and utilization [6,7].

Chemo-metallurgical methods of the group (ii).
Many methods of this group are known for recovering aluminum from high-silica alumina containing ores, concentrates, and industrial by-products. Technically suitable for ashes are those that allow to convert the compounds of aluminum, mainly mullite or metakaolinite (in low-temperature formed ashes) into acid- or alkali- soluble compounds by roasting, sintering or high-temperature hydrochemical processes [3-5].

Acid methods
One of the main advantages of acid methods is the possibility of separating the great quantities of silica in the beginning of process by leaching. But this very important advantage can be realized only in the process of direct acid leaching which is suitable for low-temperature formed ashes containing aluminum in the form of metakaolinite. In other methods, the great outlet streams of ash and auxiliary agents (limestone[8], lime, acid or other) have to be sent to the most power-consuming roasting and sintering processes which proceed to the process of leaching (Figure 1 /i/).

Alkaline methods
The current world aluminum production is based only on the alkaline technologies owing to the following advantages of these methods:
- purity and physical properties of alumina correspond to the requirements of the electrolysis process
- comparatively small stream of pulps and liquors because of high solubility of alumina in the solutions
- lack of necessity of corrosion protection for equipment and solution purification from iron

As applied to ashes, the main deficiencies of both acid and alkaline methods are the following:

1. The great streams of ash, furnace charges, cakes, pulps and liquors (Table 2).

2. Withdrawal of silica from technological process in the form of solid residue (Table 3). Contrary to silica obtained from the silicate solutions, composition and physical properties of solid residue are predetermined by the conditions of leaching therefore they can not be changed. This restricts the areas of solid residue using mainly by cement production. As has been mentioned above this application do not provide the further augmentation of ash utilization.

Ash processing for alumina production with silica recovery and utilization (Figure1, /iii/).

A great difference in solubility of mullite and compounds of free silica (Figure 2) was used for the extraction of the major part of silica from fly ash by silica pre-extraction process (SSP) [6,7]. Silica dissolved in alkaline and soda-alkaline solutions can be converted into a wide variety of valuable pure silicate products (Table 3). Extraction of the largest part of silica from fly ash decreases the outlet streams of ash, limestone, furnace charge, cake, and mud by 1.5-5.0 times (Table 2), and accordingly reduces the capital and operating costs of alumina production from fly ash.

SUMMARY

The major deficiencies of the chemo-metallurgical methods which make them non- or low-profitable for ash processing are the great outlet streams of ash and the intermediate products, and putting out silica in the form of solid residue. The deficiencies can be eliminated by means of new technologies of ash processing with the silica pre-extraction process (SPP). The main advantages of this process can be summarized in the following:

- ash is used as a polymineral source from which all of the major components including alumina, silica and iron [6] can be recovered and utilized

- silica is put out from the technological process in the form of salable chemical silicate products

- the possibility to produce a variety of valuable chemical silicate products becomes a decisive factor for improving economic showings of new technologies

- the major part of silica (50-75%) can be extracted from ash at the beginning of the technological process. This results in outlet streams decreasing and accordingly in reduction of capital and operating costs.

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Table 1. CHEMICAL ANALYSIS OF FLY ASH AND RAW MATERIALS USED BY ALUMINUM INDUSTRY (Wt. %).

Materials	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
Ash of Ekibastuz coal	28.4	59.6	5.10	1.83	1.31	0.65	0.33	0.59
Ash of WV	30.00	60.00	4.00	1.60	0.60	0.60	0.50	1.50
Bauxite:								
-low silica	41.0-60.0	0.4-8.0	0.3-30	1.0-4.0				
-high silica	43-57	12-19	6-22	2-3.5			$Na_2O + K_2O$	
Nepheline Concentrate	28-30	43-44	2-4		2-3		19 - 20	
Nepheline (Russia)	27.5	40-41	4-5			SO_3	13	
Alunite (Azerbaijan)	22	41	4			20	5	

Table 2. APPROXIMATE OUTLET STREAMS OF RAW MATERIALS AND INTERMEDIATE PRODUCTS DURING PROCESS OF ALUMINA PRODUCTION.

Material	Outlet stream, t/t Al_2O_3		Decreasing of outlet streams, times
	Direct metallurgical ash processing (S-L.S)*	Ash processing with silica preextraction (S-L.S SP)**	
Raw material	3.99 (ash)	2.63 (concentrate)	1.51
Limestone	10.27	2.06	4.98
Furnace charge	15.3	6.26	2.44
Cake	10.00	4.61	2.16
Mud	8.30	2.82	2.94

* S-L.S - soda- limestone sintering process
**S-L.S SP - soda- limestone sintering process with silica pre-extraction

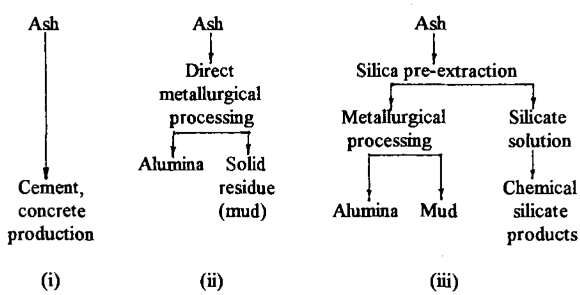

Figure1. Comparison of methods for ash utilization.
(i)-Ash uses without recovery of components. (ii)-Direct metallurgical processing of ash. (iii)-Ash processing with silica pre-extraction.

Table 3. COMPARISON OF SILICON CONTAINING PRODUCTS AND SOLID RESIDUE AFTER ALKALINE PROCESSING OF ASH BY THE DIRECT RECOVERY OF ALUMINA (ii) AND PROCESS WITH SILICA PRE-EXTRACTION (iii).

Method of coal ash processing	Silicon containing products and residue after ash processing		
	Products from solutions	Solid residue. Principal compound	Commercial uses
(ii) Direct recovery of alumina:			
- Lime-Soda Sintering		β - mud (β - Ca_2SiO_4)	cement
- Lime Sintering		γ - mud (γ -Ca_2SiO_4)	cement
- Hydrochemical high-caustic, high-temperature leaching		calcium-silica mud ($Ca[H_2SiO_4]$)	cement
(iii) Ash processing with silica pre-extraction			
- Sintering with silica pre-extraction process	a) Chemical silicate products*: SAS, SSS,SMS,CMS, SSM, SA, SC and other (45-75% of the SiO_2 total)		glasses, glazes,ceramics, enamels, color cements, zeolite, fillers, plasticizers, cosmetics, detergents and other silicon containing products
		b) β -mud (β - Ca_2SiO_4) (55-25% of the SiO_2 total)	cement

* SAS- silica alkaline solution; SSS- soda-silicate solution; SMC- sodium hydrometasilicate; CMS- calcium hydrometasilicate; SSM- soda-silicate-mixtures; SA- silica amorphous; SC- silica crystalline

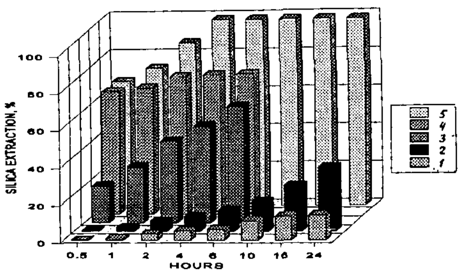

Figure 2. Efficiency of major ash compounds dissolution in alkaline solution: 1-mullite, 2-quartz, 3-ash glassy phase, 4-ash cristobalite, 5-syntetic cristobalite