THAILAND'S LIGNITE ASH AS A RAW MATERIAL FOR MANUFACTURING ALUMINA AND BYPRODUCTS BY ALKALINE HYDROTHERMAL METHOD

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Abstract

Lignite is an imperfectly formed coal which fields are widespread in many continents and countries including Thailand. It is very likely that Alkali-Lime Hydrothermal Process (ALHTP) is the only way for recovering from ash valuable products like alumina and some ot her chemicals in the future. The performed technical and economical evaluations derived from the bench-scale and pilot-plant tests data substantiate the ALHTP advantage over the sintering method being now in service with reference to aluminosilicates. Due to the ALHTP merits and flexibility, its products inventory can be modified with allowance for market conditions.

Introduction

About 20 million tons of lignite have been produced annually in Thailand [1]. 75% of that amount is combusted for power generation giving 3,600,000 tons fly ash yearly [2]. Almost the whole of the formed ash has been dumped polluting the surroundings. Taking into account that average Al_2O_3 percentage in the above-mentioned ash is about 20%, it is easy to estimate that at least 700,000 tons of aluminium oxide, called alumina, being part of ash are burried. A great many chemical methods have been proposed for processing alumina-bearing coal ash [3]. Most of these processes are distinguished by the type of either of two acidic or alkaline extractants. The acidic-leaching route is unusable for decomposition of mullite that is a significant aluminum-containing ash constituent. Both basic ALHTP and Soda-Limestone Sintering Process (SLSP) are suitable for recovery alumina and byproducts from coal ash [4].

Correlation between Hydrothermal and Sintering Processes

Examples of lignite ash composition are presented in Table 1. Comparison of ALHTP with SLSP is performed by Example 1. The foundation of classical SLSP is formation of sodium aluminate (SA) $NaAlO_2$ and dicalcium silicate Ca_2SiO_4 as a result of high temperature (1220-1

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Table 1. Examples of lignite ash composition taken form the data of Electrictity Generation Authority of Thailand (EGAT) [1]

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	SO_3	Total
Example 1(wt%)	44.0	23.0	14.0	6.5	3.0	1.7	1.5	93.7
mol/mol Al_2O_3	3.25	1.0	0.39	0.51	0.21	0.08	0.08	
Example 2(wt%)	51.0	19.5	17.0	2.0	3.0	1.7	1.5	95.8
mol/mol Al_2O_3	4.45	1.0	0.56	0.19	0.25	0.10	0.10	

Table 2. Comparative ALHTP and SLSP indexes with reference to different ASBRM

Process	ALHTP	ALHTP	ALHTP	SLSP
ASBRM	Coal ash	Anorthosite	Nepheline	
		Input per 1 ton Al_2O_3		
ton:				
ASBRM	4.47	4.38	3.96	3.93
Limestone	5.65	4.09	3.62	7.92
NaOH	0.36	n.s.*	0	0
Water	12.34	n.s.*	40.0	26.0
Power (kWh)	1500	n.s.*	600	1050
Fuel (GJ)	27.3	19.25**	36.8	60
($US)[10]	23.55	16.61	31.75	129.35
type	coal	coal	coal	oil
		Input per 1 ton Al_2O_3		
Caustic soda	0	0	0.97	0
Soda ash&Potash	0	0	0	1.08
Calcium silicate-bearing sludge	7.56	6.49	4.66	5.94
containing intermediate	TCHA***	SHA	SHA	SA

*not specified.

**Fuel input for SLSP as applied to anorthosite is reported to be 65 GJ/ton Al_2O_3 [9] that is estimated as $US 101.98 using gas and $US 140.13 using crude oil [10].

*** Tricalcium hydroaluminate $Ca_3Al_2(OH)_{12}$

400°C) solid-phase interactions between aluminosilicate like mullite, glassy phase, soda and limestone [5]. Simplified molar balance (SMB) of SLSP is diagrammatically shown in Figure 1.

The sinter obtained is leached by process water and slurry formed is separated into aluminate solution and Ca_2SiO_4-containing sludge. The latter is water washed and used for construction materials production (CMP). The solution is desilicated and then carbonized by cooled and cleaned flue gases . As a result, alumina hydrate $Al(OH)_3$ is precipitated and soda-sulfate solution (SSS) is depleted. $Al(OH)_3$ is calcined to alumina and SSS is evaporated to crystalliz the reusable soda hydrate and to remove sulfate residue from the process.

In contrary to SLSP, the classical ALHTP is based on formation of sodium-calcium hydrosilicate (SCHS) $NaCaHSiO_4$ and conversion of aluminosilicate into aluminate solution by raw material digestion. This procedure is carried out in the presence of caustic solution and lime at temperature 250°C and higher [6]. SMB of classical ALHTP is shown in Figure 2. Aluminate solution is consequently

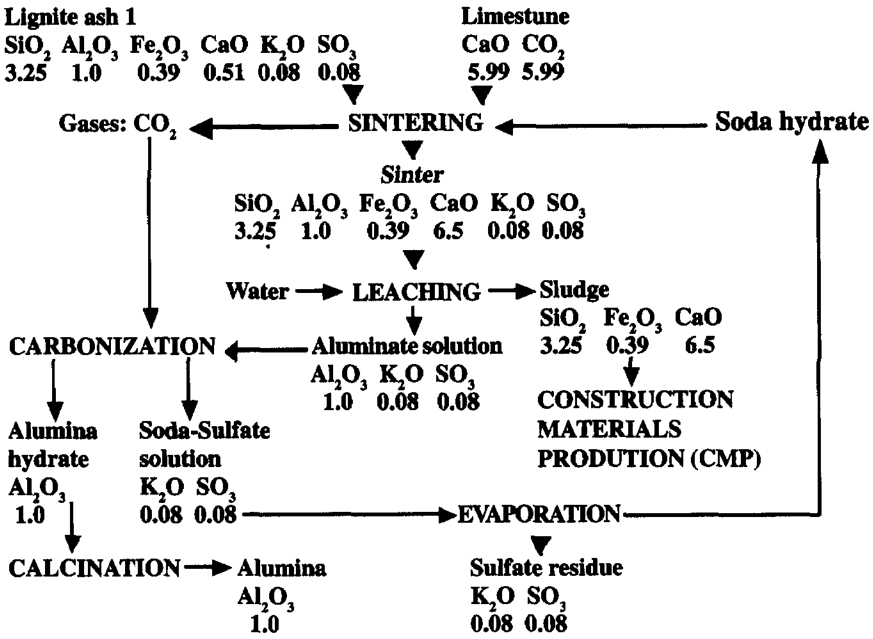

Figure 1. Simplified molar balance (SMB) of lignite ash utilization by SLSP

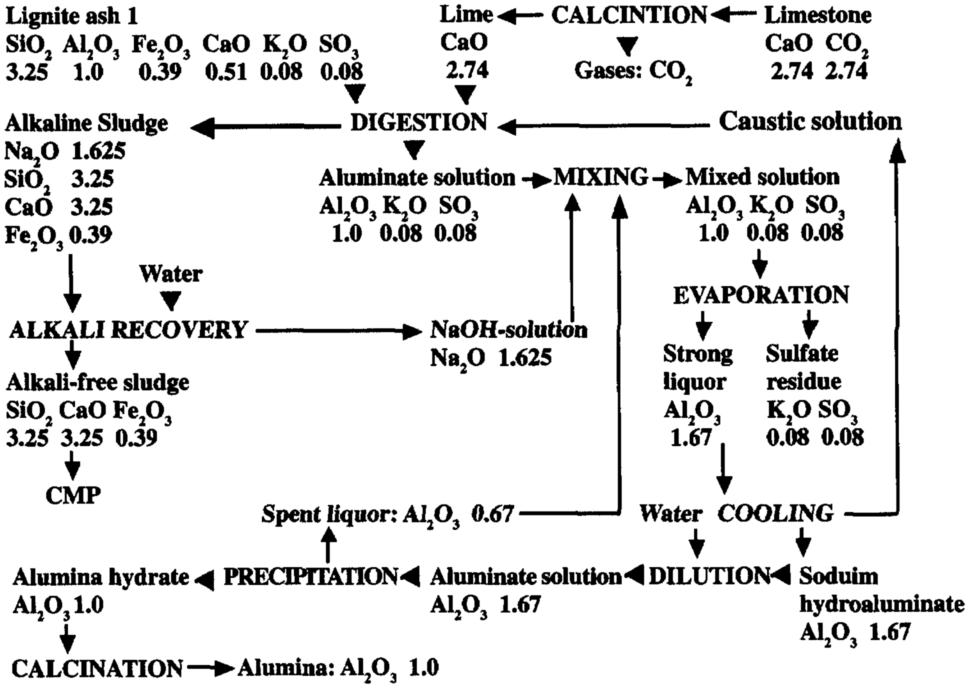

Figure 2. SMB of lignite ash utilization by the classical ALHTP

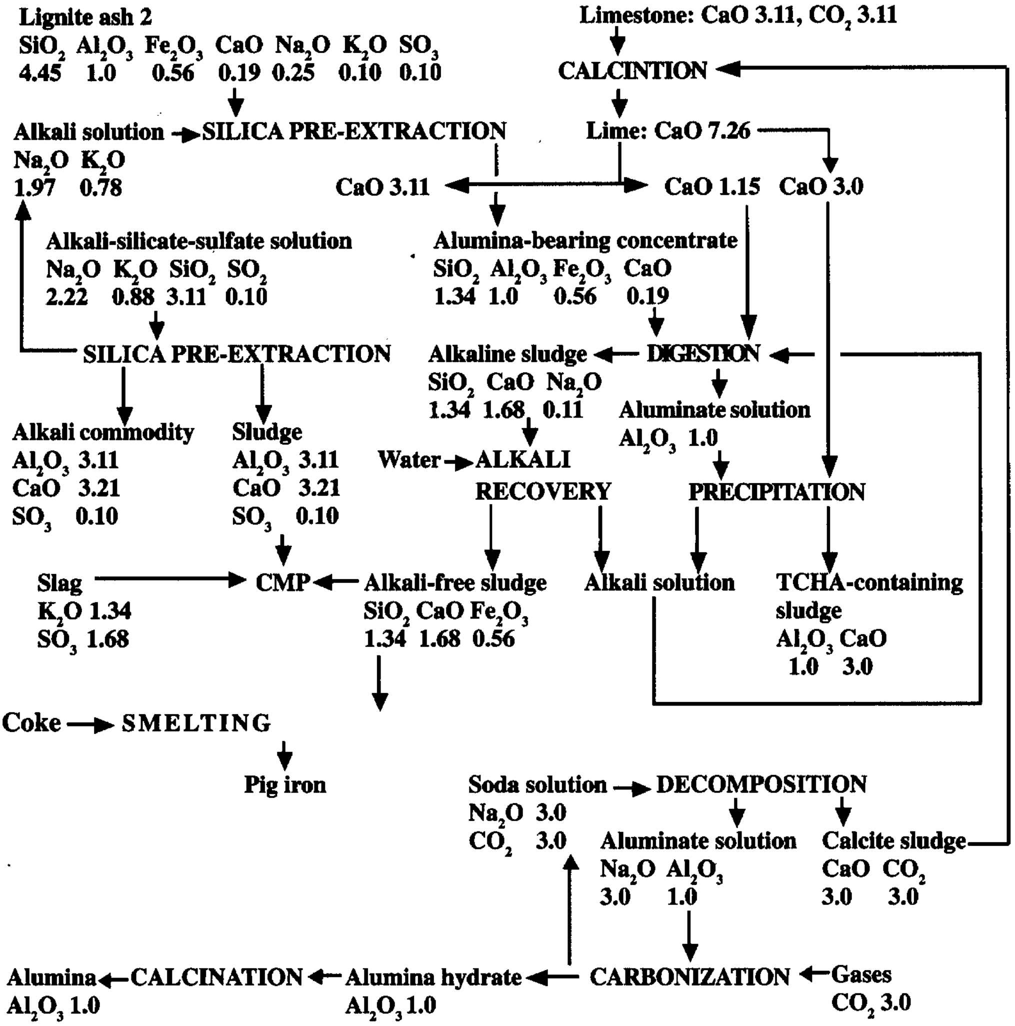

Figure 3. SMB of lignite ash utilization by the modified ALHTP

desilicated, evaporated to Na_2O concentration 550 g/l, then cooled and sodium hydroaluminate (SHA) $Na_2Al_2O^4$, (2.5-3)H_2O is crystallized [7]. The crystals obtained can be used as a final chemical product or processed into $Al(OH)_3$. The sludge containing SCHS is treated with process water at 80-90°C giving alkali-free remainder and reused alkali liquor.

Both ALHTP and SLSP compared ways were economically estimated. Coal ash [8] and other aluminosilicate-bearing raw materials (ASBRM) like anorthosite [9] and nepheline [6] have been considered. The data obtained are given in Table 2. As is evident from the tabular data, principal streams are characterized by the bulk of feed materials and dumped sludges because of the high SiO_2 content (44-53%). Fuel inputs have the most impressive differences between ALHTP (19-37 GJ/ton Al_2O_3) and SLSP (60-65 GJ/ton Al_2O_3). These consumption items expressed in US dollars are as followed: \$16.6-31.8 for ALHTP and \$102-140 for SLSP.

Correlation made by both thermal and monetary dimensions favours ALHTP. Its fuel consumption advantage is caused by the more perfect systems of transferring and recovery of heat as well as lower temperatures used for extraction of alumina. The kind of fuel combusted, not its consumption only, determines the fuel cost. In this regard, preference should be also given to ALHTP that is base d on indirect use of fuel gases heat for the feed stock decomposition. This procedure is carried out through steam generation as followed: fuel—>FIRE BOX—>fuel gases—> BOILER—> steam—>HEAT EXCHANGER. Therefore, coal as the least expensive type of fossil fuel [10] can become the most profitable source of heat due to ALHTP commercialization. The contrastable sintering method predetermines fuel combustion directly in the sintered blend. Therefore, mixing coal with ASBRM, limestone and soda leads to reducing percentage of combustible part of the prepared charge that becomes nonflammable. Consequently, only more expensive ash-free kind of fuel like gas and oil is acceptable for SLSP heat supply. Lower cost of coal used for implementing ALHTP causes saving, in comparison with SLSP, at the minimum \$70/ton Al_2O_3. The fuel consumption (FC) in ALHTP operation is close to that in the most efficient Bayer process.

In spite of obvious merits of ALHTP, its layout can be further improved with considerations of lignite ash composition features.

The Ways for ALHTP improvement

Fe_2O_3 content in some Thailand's lignite ashes is higher than 15% [1]. This feature makes possible to bind both iron and silicon in alkali-free calcium-ferrous hydro-garnet (CFHG) $Ca_3Fe_2(SiO_4)m(OH)_{12-4m}$ [4,6]. Due to CFHG formation, sodium percentage in the sludge is decreased and alkali recovery step of the process is reduced.

It is reasonable to subject coal ash containing less than 3-5% CaO to preliminary silicon extraction (PSE) into caustic solution [3, 11]. This procedure carried out at 90-100°C and Na_2O concentration 100-200 g/l allows to reduce the digested material stream removing up to 70% SiO_2. An obtained solid residue, so-called alumina-enriched concentrate, can be digested using double-flow layout that provides the separate heating of both feedstock and lime alkaline slurry for fouling mitigation [12].

Tricalcium hydroaluminate (TCHA) $Ca_3Al_2(OH)_{12}$ can be precipitated from ALHTP aluminate solution instead of SHA at Na_2O concentrations about 200-300 g/l which is significantly lower than concentration required for SHA crystallization (*550* g/l). In this case, Na2O concentration gradient of the process is reduced and steam input decreased, though, heat consumption for calcination of extra limestone streams must be higher. This way was pilot-plant tested [8]. Coal ash ground with lime and caustic liquor was pumped through autoclave at the slurry rate of 30 1/hr. The digestion conditions were as followed: temperature 300°C, Na_2O concentration 300 g/l, residence time 10 minutes. 80% Al_20_3 yield was obtained. As may be seen from Table 2 the limestone input 5.65 tons per 1 ton Al_20_3 for this modification using TCHA precipitation exceeded the same index for ALHT processing anorthosite (4.09 tons) and nepheline (3.62 tons). It was also asserted that ALHTP for ash utilization has been under development for about 10 years at Alcoa's pilot plant [3]. The best decision to be followed is found on the basis of raw material composition and local conditions.

All innovations described above are embodied in Figure 3 covering SMB for ALHT-processing lignite ash of composition 2 low in calcium (CaO 2%) and high in iron (Fe_2O_3 17%).

The final solid product can be enriched with trace elements [13]. Specifically, a sample of Asian lignite (Kazakhstan) containing scandium 100 g/t, yttrium 100 g/t and lanthanum 100 g/t was subjected to alkaline digestion. The resulting residue percentages were as followed: scandium 450 g/t, yttrium 200 g/t and lanthanum 900 g/t being of commercial interest for production of rare-earth metals [14].

The most complete pilot-plant tests of ALHTP extended over 30 years have been carried out in Russia's National Research Ins titute of Aluminium and Magnesium (VAMI) [4, 6, 16]. The units for preparation, heating and digestion of raw material, flashing and filtration of slurry, washing cake, aluminate solutions desilication, evaporation and cooling, as well as SHA precipitation have been examined. Al_20_3

yield in the course of ASBRM hydrothermal processing was so much as 88-92%.

Discussion and Conclusions

Application of ALHTP for lignite ash utilization can simultaneously solve energetic, resources and environmental problems of Thailand. The point is that Thailand's lignite would be both raw material and fuel; in so doing ash dumping must lost any necessity. Total combination of these advantages is very important for Thailand lacking commercial deposits of bauxite. Moreover, it was determined that the direct operating costs are almost the same for both plant based on ALHTP and alumina refinery processing bauxite by the Bayer method [15]. Besides alumina hydrate and alumina, other valuable chemicals can be produced through ALHTP commercialization. Among these products are SHA, TCHA, silica-gel, calcite and CFHG. SHA is an effective coagulant for water purification as well as additive to mixtures for manufacturing drilling mud, waterproof concrete, zeolites, paper and cardboard [7]. The main TCHA field of usage is production of special high-alumina high impact, rapid-setting, straining and refractory cements [17]. As to CFHG, it should be processed into pig iron and calcium-silicate slag. Needless to say about handling $Al(OH)_3$ and $A1_20_3$ since both have been world wide processing into aluminium, refractories and burning retardants. The possibility to concentrate rare-earth elements in the remainder after double digestion of lignite ash must not be ruled out. ALHTP flexibility implies that its layout may be easily changed to turn out one or another product as the consumers' requirements. It should be noted that the lignite fired waste is a fine, loose and mining-free feedstock to give an additional advantage for its processing in Thailand.

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