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Production of alkali-free alumina

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A survey will be presented on various methods for the preparation of alkali-free aluminas. Special attention will be focused to the hydrochloric acid-alumina process, which has been proven by industrial installations. According to described process alternatives $AlCl_3 \times H_2O$, produced by means of leaching aluminum with hydrochloric acid, becomes thermally decomposed into HCl vapor yielding regenerated hydrochloric acid and high purity reactive aluminum oxide powders. The physical and chemical properties of produced aluminas, which in statu nascendi contain up to 85 % alpha-alumina will be discussed.

1. INTRODUCTION

Various processes have been proposed for the production of high purity alumina. Aluminas prepared by the Bayer- or similar processes contain alkali ions, which can't easily be removed to concentrations, which would not effect the quality of sintered alumina products [1]. Due to these facts there is an interest for processes yielding alkali-free aluminas. Several methods have been proven on laboratory scale [2], but only a few are of commercial importance. Among these processes is the hydrochloric acid-alumina process, which is reported upon later in this paper.

2. PROCESS CHARACTERISTICS

High purity aluminum is frequently used as raw material for the production of alkali-free aluminum oxide powders. A survey presenting processes for the preparation of alkali-free alumina is given in Figure 1.

Aluminum may directly be oxidized by oxygen or air to alumina. This reaction occurs at high temperatures (molten state) yielding mixed reaction products consisting of gamma-, delta- and alpha-alumina [3]. Steam reacts at elevated temperatures very fast with aluminum without previous metal activation yielding high purity aluminum oxide phases [4]. The phase diagram of the system alumina-water is given in Figure 2.

Bayerite is the only stable trihydroxide at the absence of impurity ions. Among the monohydroxides boehmite is stable at low and diaspore at high vapor pressure. Within

Reagent	Process	Reference
OXYGEN	DIRECT OXIDATION (fused metal, O_2/H_2-flame reaction)	(3)
WATER	VAPOR PRESSURE (autoclave)	(4,5,6,7)
	ACTIVIATION (mercury salts)	(8)
	ELECTROLYSIS (spark discharge)	(9,10)
ORGANIC R.	Al-ORGANIC COMPOUND DECOMPOSITION (Al-aethylate, Al-propylate a.o.)	(11)
INORGANIC R.	Al-SALT DECOMPOSITION (hydrochloric acid alumina process)	(12,13,17, 20,21)

Fig. 1. — Processes for the preparation of alkali-free alumina from aluminum

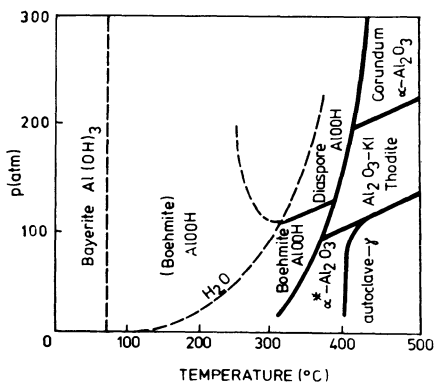

Fig. 2. — Temperature vs pressure plot for the hydrothermal formation for aluminum-hydroxides and oxides ▶

the area of unsaturated steam active alpha-alumina [5] and autoclave gamma are formed. At moderate pressures the phase alumina KI [6] is stable, which due to its anion layering arrangement has to be inserted between gamma-and alpha-aluminum oxide. At high steam pressure the only stable phase is alpha-alumina.

In order to react aluminum and water without pressure the metal has to be activated by means of dipping it in a weak solution of a mercury salt to be followed by a rinsing procedure [8].

High purity $Al(OH)_3$ or Al_2O_3 may be prepared by electrolytic means employing aluminum electrodes. Furthermore gamma-alumina may be produced by spark discharge under water [9], [10].

Reactions with organic reagents leading to the formation of e.g. Al-methylate, Al-aethylate, Al-propylate a.o., yield on hydrolyzing high purity $Al(OH)_3$ [11].

Finally reactions of aluminum with inorganic reagents; e.g. acids lead to the formation of metal salts. Aluminum salts such as $AlCl_3$, $Al(NO_3)_3$, $Al_2(SO_4)_3$ or alum a.s.o. have been converted to $Al(OH)_3$ and Al_2O_3 by various processes [12], [13], [17], [20], [21].

The physical and chemical properties of the formed alumina depends on the nature of the salt being decomposed and the reaction conditions. As an example for above mentioned reactions the hydrochloric acid-alumina process will be discussed in detail.

3. THE HYDROCHLORIC ACID-ALUMINA PROCESS

Plants have been built for two alternatives of the hydrochloric acid-alumina process. High purity + 99,9% aluminum, which has been used as raw material for both process

alternatives, becomes dissolved within hydrochloric acid yielding aluminum chloride solutions and hydrogen gas [12], [13].

The process flow sheet for the first process alternative of the hydrochloric acid-alumina process is given in Figure 3. This process is characterized by an evaporation step, where water and free HCl are driven off by indirect heating means yielding a weakly acid concentrated but nearly saturated aluminum chloride solution. Resulting aluminum chloride solution becomes neutralized by means of recycled aluminum oxide powder.

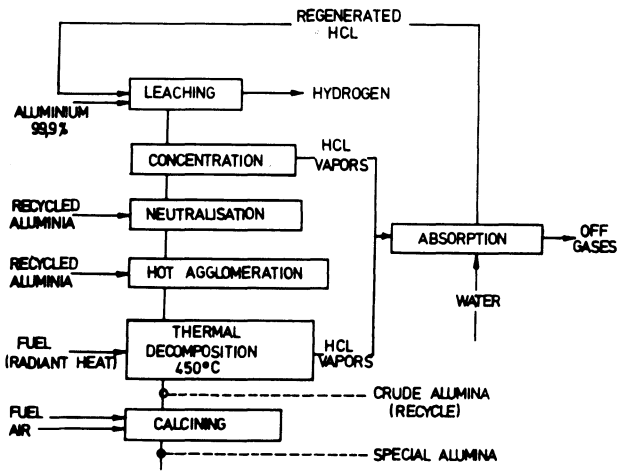

Fig. 3. — HCl-alumina process. Low temperature thermal decomposition of $AlCl_3.x\ H_2O$

A combined process step of mixing, drying and hot agglomeration of $Al(OH)_3$, $AlCl_3 . 6\ H_2O$ and recycled Al_2O_3 occurs in the upper part of a multiple hearth furnace. Subsequent decomposition and transition reactions take place at temperatures around 450 °C. The reaction gases are merged with the HCl vapors originating from the evaporation section, pass through an absorption column, become dissolved in water and form regenerated hydrochloric acid, which comprises all HCl used within the process. A part of produced alumina, which is discharged at the bottom of the reactor is being recycled for neutralization and hot agglomeration. According to this process alternative amorphous aluminas are formed. A BET measurement yielded a specific surface area of 135 m^2/g. For this specific process a plant for the production of 25 kg alumina per hour has been built.

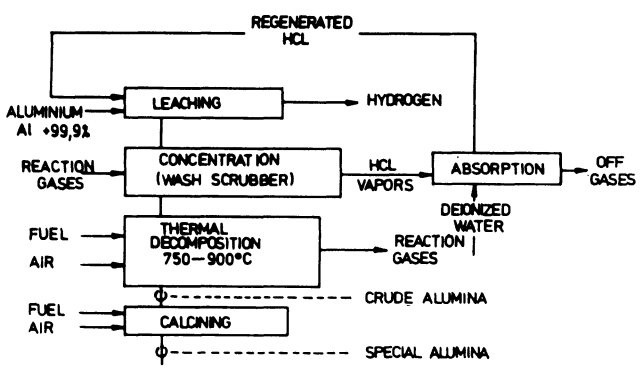

Fig. 4. — Fast heat hydrochloric acid-alumina process. Thermal decomposition of $AlCl_3.x\ H_2O$

According to the second process alternative, which is called fast heat hydrochloric acid-alumina process (Fig. 4), the aluminum chloride solution becomes directly fed to a multi purpose recuperator. By means of direct contact with the heat of the reaction gases water and hydrochloric acid evaporate. Resulting concentrated aluminum chloride solution, which also contains solid alumina particles from the roaster off gases, becomes pressurized before it is sprayed into the directly fired roaster furnace. The decomposition reaction yielding alumina and HCl vapors occurs within a few seconds at temperatures, which may be varied between 750 and 900 °C.

Produced alumina becomes discharged at the bottom of the furnace. The alumina fines of the hot reaction gases become removed by a cyclone and the scrubbing action of the recuperator. From the recuperator the vapors go to an absorber, where hydrogen chloride gas becomes dissolved in deionized water yielding regenerated hydrochloric acid. The exhaust gases from the absorber, which are practically free of HCl and solid particles, are vented by a fan to a stack and atmosphere. The closed acid loop is in excess of 99 % efficient as a recovery device.

A plant producing in excess of 60 kg alumina per hour has been in operation for one year by now and is presented in Figure 5.

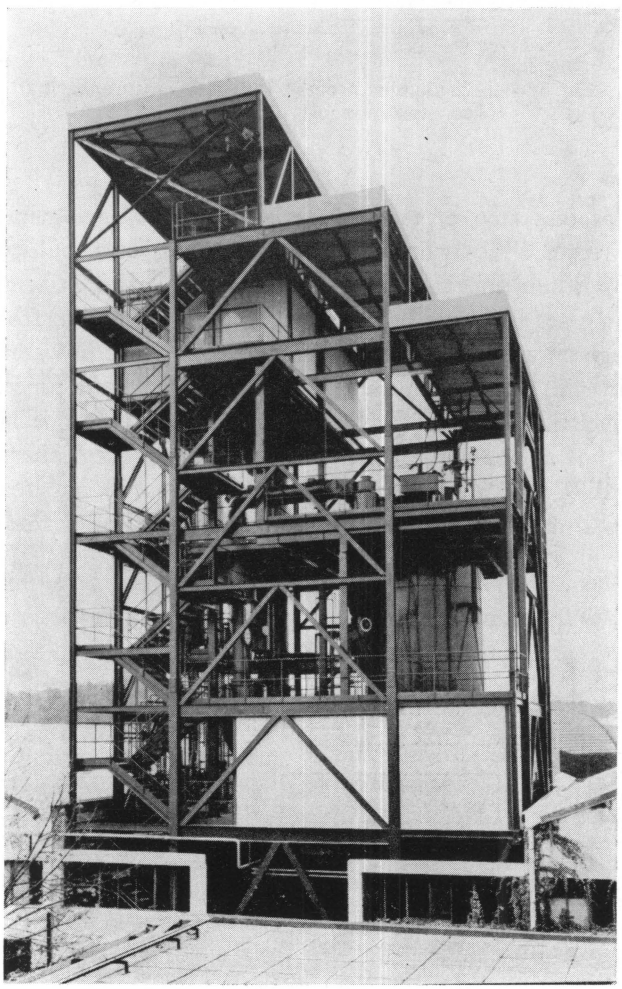

Fig. 5. — Fast heat hydrochloric acid-alumina process. Plant for the production of high purity alkali-free alumina (capacity 400 metric tons of alumina per year)

4. PROPERTIES OF ALUMINA PRODUCED ACCORDING TO THE FAST HEAT HYDROCHLORIC ACID-ALUMINA PROCESS

The material properties of aluminum oxide powders, produced according to the fast heat hydrochloric acid-alumina process depend to the greatest extent on used raw material, engineering lay out and plant operation. The chemical analysis have been carried out by using spectrographic and atomic absorption techniques. The results are given in Figure 6.

Fe	< 50 ppm	Ti	< 10 ppm	Mo	< 3 ppm	Na	not det.
Si	< 50 ppm	Mn	< 10 ppm	Ga	< 3 ppm	V	not det.
Ca	< 50 ppm	Cu	< 5 ppm	Co	< 3 ppm	K	not det.
Zn	< 20 ppm	B	< 5 ppm	Mg	< 10 ppm	Cl*	< 30 ppm

Fig. 6. — Fast heat hydrochloric acid-alumina process. Chemical purity analysis of produced alumina (Cl* value for pure alpha-alumina)

The crystallographic modification of produced aluminas depend to the greatest extent on the maximum temperature of thermal decomposition, which has been varied within the temperature range of 750 to 900 °C.

Figure 7 indicates that within the temperature range of 750 to 850 °C gamma-alumina is most frequently formed. At higher temperatures alpha-alumina is the predominant crystallographic modification. The fraction of alpha-alumina formed may be influenced by the maximum temperature of thermal decomposition and to a minor extent by selecting specific operating conditions. The industrial plant, which has been described above, produces alumina consisting of up to 85% alpha-alumina. This fact is remarkable for the given process, since the reaction temperature is rather low and the time of retention is extremely short.

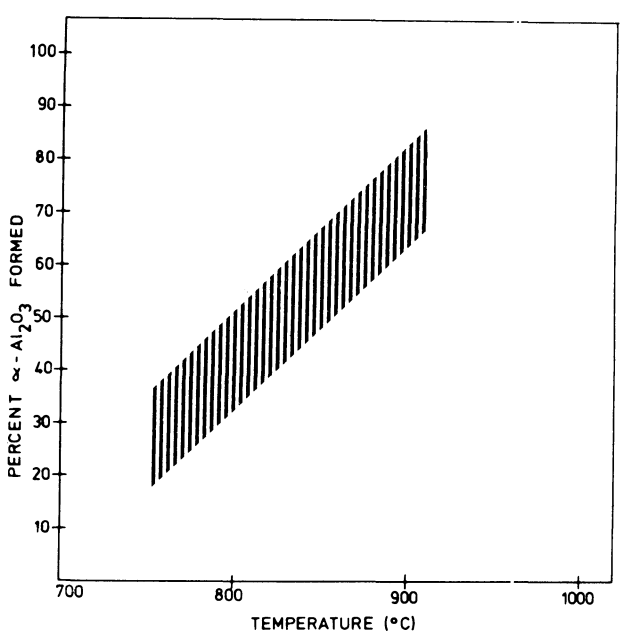

Fig. 7. — Fast heat hydrochloric acid-alumina process. Percent of alpha-alumina formed as a function of temperature

Produced alumina contains fractional parts of gamma-alumina, which consist of fine alumina powder of poor crystalline state. The particle size of gamma-alumina, which has been investigated by X-ray diffraction techniques was smaller than 500 Å. The BET surface area amounts 50-60 m^2/g. The X-ray diffraction peaks of gamma-alumina were too broad and not well defined and made an exact determination of different gamma-modifications impossible.

Tests carried out for several hours in boiling water indicated no rehydration for 85% alpha-alumina.

It is interesting to note that gamma-alumina produced according to the fast heat hydrochloric acid-alumina process becomes transformed into alpha-alumina at moderate temperatures around 900 °C. In comparison with most gamma-aluminas prepared according to various other processes, a few hours at temperatures around 1 200 °C are required for complete gamma- to alpha-alumina phase transformation [14], [15], [16].

Figure 8 shows the time dependance of phase transformation of gamma- to alpha-alumina at various temperatures. The rate of structural transition has been investigated by means of quantitative X-ray phase analysis. The structural transition of gamma- to alpha-alumina follows zero-order kinetics, which is in accordance with data obtained by C. P. Steiner et al. [14].

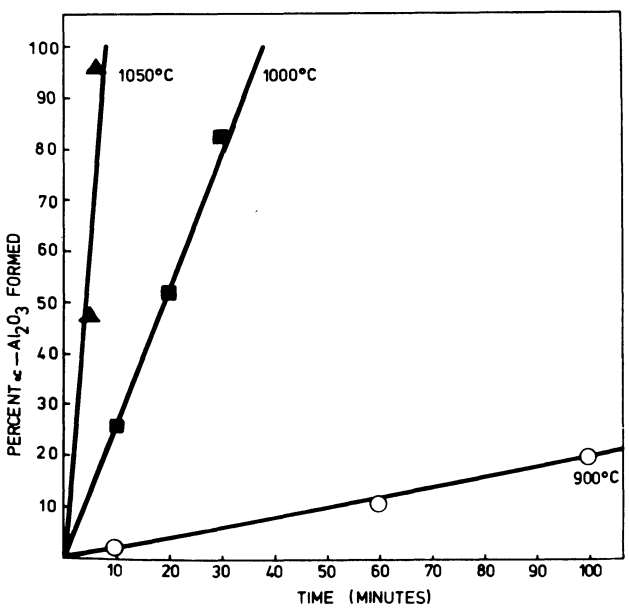

Fig. 8. — Fast heat hydrochloric acid-alumina process. The gamma- to alpha-alumina phase transformation as a function of time for various temperatures

The activation energy of 75 kcal/mol associated with the kinetics of gamma- to alpha-alumina phase transformation of the present study disagrees with the activation energy of 116 kcal/mol reported by C. P. Steiner et al. The activation energy is however of the same order of magnitude observed by Clarke and White [15], who found an activation energy for this transformation of 79 kcal/mol.

Alumina (85% alpha-alumina) produced by the fast heat hydrochloric acid-alumina process exhibits a high reactivity and an apparent density of 256 g/l. This density may be increased up to approx. 500 g/l by means of mechanical working leading to the deagglomeration of alumina particles. The primary size of alpha-alumina particles has been

detected by means of X-ray techniques and ranges from about 1 000-1 500 Å. The BET surface area of pure alpha-alumina amounts to 9-15 m^2/g.

A heat treatment for 90 min. at 1 400 °C decreased the BET surface area to 2 m^2/g, thus increasing the apparent density after a short deagglomeration procedure to 750 g/l.

Grain growth of alumina particles on heating occurs due to the high chemical purity of the material rather slow. The influence of temperature and retention time on the average particle size (calculated from BET measurements) is given in Figure 9. The kinetic of this reaction is definated by the equation $D \alpha t^x$ and shows herewith similar material characteristics as high reactive alumina prepared from freeze dried alum [17].

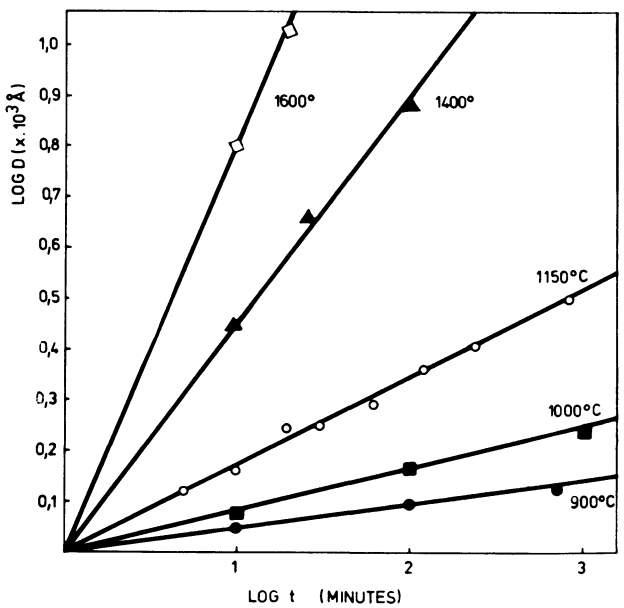

Fig. 9. — Fast heat hydrochloric acid-alumina process. Log plot of particle size D vs log time for alpha-alumina (data for particle size D 10^3 Å obtained from BET measurements)

5. DISCUSSION

It is most interesting to note that alpha-alumina may be formed at temperatures above 700 °C employing the fast heat hydrochloric acid-alumina process. In comparison alumina formed by means of a plasma beam at much higher reaction temperatures yielded only a mixture of gamma and delta-alumina [18].

On dehydrating aluminum hydroxides and on the thermal decomposition of most aluminum salts, temperatures around 1 200 °C are required in order to form alpha-alumina. Exceptions of this rule are however known. The diaspore to alpha-alumina phase transformation occurs at temperatures around 400 °C. G. Ervin [19] recalls the relative strong tendency of the diaspore to alpha-alumina structural transformation to be directly related to crystallographic similarities of the compounds because the layering arrangement of diaspore may be directly related to the oxygen layer of alpha-alumina.

Torkar [20] having similar thoughts in mind investigated the thermal decomposition of AlF_3 within a temperature range of 450-700 °C. Low HF partial pressures within the reaction chamber led to the formation of active alpha-alumina. Whenever the HF partial pressure was high, fluor containing gamma-aluminas have been formed.

Therefore the condition under which the thermal decomposition of aqueous aluminum chloride solution has been carried out may be related to the thermal decomposition characteristics of AlF_3. The first solid phase, which occurs on the thermal decomposition of $AlCl_3$ aqueous solution is $AlCl_3 . 6 H_2O$ crystallizing hexagonal in a biomolecular rhombohedral cell. $AlCl_3 . 6 H_2O$ as well as alpha-alumina crystallize in the space group D^6_{3d} (R3c).

In case the thermal decomposition of $AlCl_3 . 6 H_2O$ occurs very fast, alpha-alumina is formed according to following relation:

$$2 AlCl_3 . 6 H_2O \rightarrow \text{alpha-}Al_2O_3 + 6 HCl + 9 H_2O$$

Scanning electron micrographs (Fig. 10) indicate that the external shape of formed $AlCl_3 . 6 H_2O$ particles is not effected by the decomposition reaction. The particles consist of pseudomorphic platelets (Fig. 10). Even after a heat treatment of 30 min. at 1 400 °C the external shape of the platelets is retained as indicated in Figure 11.

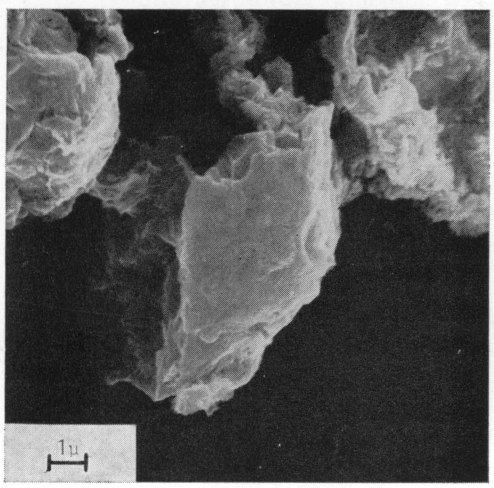

Fig. 10. Fast heat hydrochloric acid-alumina process. Scanning electron micrograph of alumina formed by the thermal decomposition of $AlCl_3$-solutions (x 6 000)

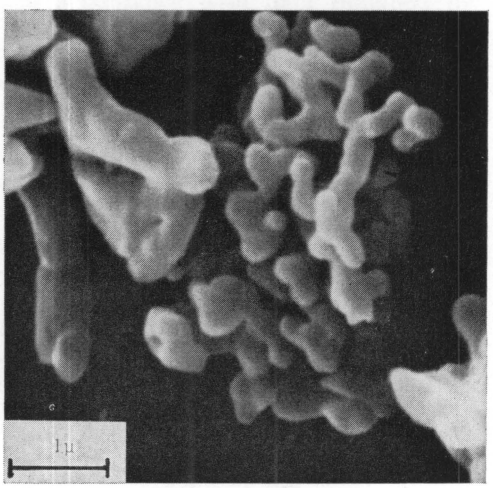

Fig. 11. — Fast heat hydrochloric acid-alumina process. Scanning electron micrograph of alumina formed by the thermal decomposition of $AlCl_3$-solutions, after a heat treatment for 30 min at 1400 °C (x 20 000)

Similar to the example mentioned above the reaction favours the formation of the hexagonal packed oxygen layer of alpha-alumina in comparison to the cubic layering arrangement of gamma-alumina.

In case the thermal decomposition reaction of $AlCl_3 . 6 H_2O$ does not occur fast enough permitting HCl to escape, e.g. at lower temperatures, the formation of gamma-alumina containing considerable amounts of residual chlorides is favoured. Therefore the behaviour is similar to the thermal decomposition of AlF_3 leading to the formation of HF stabilized phases.

On heating gamma-aluminas containing chlorides, alpha-alumina is formed at temperatures around 900 °C. This observation may be related to the fact that HCl is driven off from the gamma-alumina lattice, which becomes unstable and undergoes a structural transformation according to the equation of reaction:

$$Al_{22}\square_2O_{30}(OH)_3Cl_3 \rightarrow 11\ Al_2O_3 + 3\ HCl$$

$\square$..... vacancy

into the stable alpha-alumina phase.

6. SUMMARY

It may be concluded that the fast heat hydrochloric acid-alumina process provides a new method for the production of high purity active alkali-free aluminas on an industriel basis. By means of a short subsequent thermal treatment it is possible to produce reactive high purity alkali-free aluminas with a wide range of particle size distributions and specific chemical properties for different applications.

7. ACKNOWLEDGEMENTS

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