

THE THERMAL DECOMPOSITION OF THE CARBONATE REACTION PRODUCTS

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Abstract

The complex thermal analysis was used in the investigations of the carbonate reaction products in the residue after Al leaching from calcium aluminate – $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and Selfdisintegrated Powder. The conversion of Al was calculated basing on a content of Al in the pregnant solution as well as in a residue obtained from the kinetic investigations. The third method of measurements of a conversion of Al was presented and discussed. Results show, that the proposed method can be used for conversion estimations with 95% of confidence level as well as for the detection of carbonate products and is useful for an interpretation of the new approach for kinetic mechanism of Al leaching.

Keywords: carbonate reaction products, decomposition

Introduction

The modern extractive metallurgy of Al is dominated by Bayer's method where aluminium is converted into sodium aluminate solution from bauxite under the higher temperature and pressure conditions by sodium base. In Selfdisintegrated Grzymek's Method [1] raw materials are sintered at 1350°C where two main compounds such as calcium orthosilicate ($2\text{CaO}\cdot\text{SiO}_2$) and calcium aluminates ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ or $\text{CaO}\cdot\text{Al}_2\text{O}_3$) are synthesized. After cooling, sinter disintegrates into the fine powder called Selfdisintegrated Powder (*SDP*). The recovery of Al from *SDP* is carried out in the leaching process with an aqueous sodium carbonate reactant. The general notation of the heterogenous chemical reaction is as follows:



The conversion of Al from the calcium aluminates depends mainly on a key parameters such as mineralogical composition of *SDP*, time and temperature of

leaching, concentration of reactant, methods of stirring and etc. Conversion of Al is usually calculated by the chemical analysis of a content of Al in the sodium aluminate solution or by the chemical analysis of a residue.

As it can be seen from Eqs (1) and (2), if the conversion higher the contents of Al in a solution higher and the higher the calcium carbonate products in residue. Therefore, using the complex thermal analysis is possible to investigate the decomposition of the carbonate reaction products as well as the temperature range of endothermic effects, particularly when is a need to explain some problems appearing during leaching of Al from different type of *SDP* synthesized by sintering or melting procedures. These problems were presented at first in previous paper [2, 3] where was demonstrated that carbonate products have been existed in the form of vaterite, aragonite and calcite modifications of CaCO_3 . Nevertheless, leaching in the liquid–solid system is more complicated when the additional chemical reactions follow between other compounds of the *SDP* and the sodium aluminate solution [4, 5]. Thus, proposed method was used for calculation of a conversion of Al during leaching from the best leachable calcium aluminate i.e. $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ as well as for detection of the carbonate reaction products.

Experimental

Material

For the needs of this study, a sample of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ was synthesized at 1350°C . The resulting material was grinding, screening below $60\ \mu\text{m}$ and was analyzed chemically and by XRD method. The size distribution of the original sample was obtained by a Sartorius Analyzer. The average size of grain was $16\ \mu\text{m}$. The chemical analysis revealed that is no free CaO and the content of Al_2O_3 amounts 50.9%. X-ray diffraction analysis identified only $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$.

The second material, typical for an industrial *SDP*, was synthesized at the same temperature in the laboratory electric furnace. The content of Al_2O_3 was 15.2%. The $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ and $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ with traces of $\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ were also detected by X-ray technique. About 0.5% of free CaO was verified by the chemical analysis.

Equipment and procedure

The experiments were carried out with a glass reactor of a 500 ml heated by the use of an electric heater. The agitation inside the reactor was obtained by a magnetic stirrer. For every experiment the reactor was filled with 200 ml of

leach solution which had been prepared from reagent grade chemicals. The reactor was heated to the desired temperature. Once this temperature was reached, 10 g of solid sample of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ or *SDP* was added to the reactor. At regular intervals, small samples of the leach solution were drawn from the reactor. The samples were then determined for Al by the complexometric titration and the conversion of Al that has come into the solution was calculated. Next, the experiments were repeated and the solid residues after each intervals was collected and was washed with distilled water. The remaining Al was then chemically determined.

The residue sample were next tested by the complex thermal analysis with Paulik and Paulik as well as SETARAM equipments with the following parameters: heating rate – $10 \text{ deg}\cdot\text{min}^{-1}$, atmosphere – air, reference material – $\alpha\text{-Al}_2\text{O}_3$, crucible – Pt and heating rate $\text{deg}\cdot\text{min}^{-1}$, atmosphere – argon, respectively. Conversion calculations were based on the weight changes between 650 and 950°C.

The phase description of residues and calcinated carbonate products was determined by PHILIPS X-ray apparatus.

Results and discussion

The chief leaching experiments have been carried out with the following parameters:

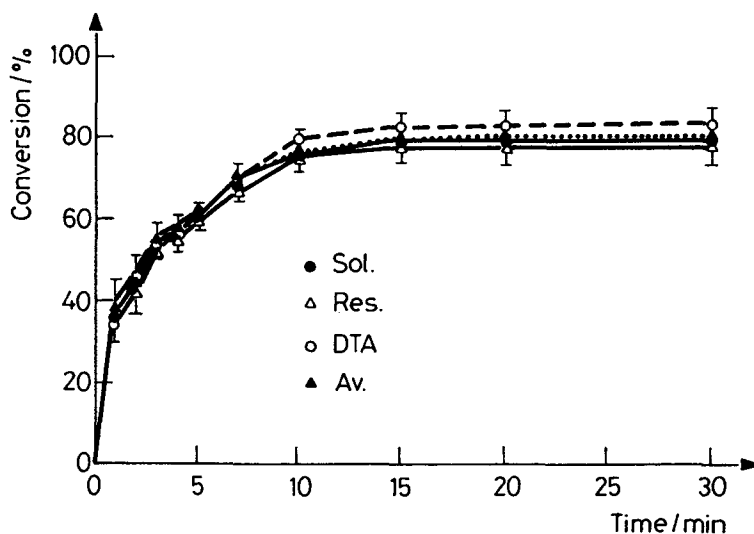
- (i) temperature (20, 40, 60 and 80°C),
- (ii) reactant concentration (50 g of $\text{Na}_2\text{CO}_3 \text{ l}^{-1}$),
- (iii) solid-liquid ratio (1:20),
- (iv) Al content in solid (2.69 g), and
- (v) agitation speed ($600 \text{ rev}\cdot\text{min}^{-1}$).

As it can be seen from Table 1 and Fig. 1, conversion of Al gauged according to considered methods exhibited a high common agreement. The confidence interval calculated with 95% of confidence level according to Dean and Dixon [6] was ranged from ± 2.34 to ± 7.67 and depends on a distribution between maximum an minimum values obtained by individual methods. The best agreement ($s_d = 1.05$) was reached for 5 minutes of leaching. The differences between conversion of Al at first minutes and last minutes of measurements, especially for DTA method, were caused by various products of chemical reactions and will be discussed afterward. The chemical analysis of residue revealed lower conversions of Al (about 2.4% in average) than the determined from solution.

The DTA curves obtained by Paulik & Paulik System (Fig. 2), demonstrate the thermal decomposition of residues and three peaks can be distinguished. The chief endothermic peak related with the decomposition of calcium carbon-

Table 1 The conversion of Al calculated by three considered method

Time/ min	Conversion of Al/ %			Average/ %	Std.dev./ S_d
	Solution	Residue	DTA		
1	40.1	38.8	34.2	37.7	3.48
2	47.6	43.2	42.3	44.4	3.13
3	56.5	53.3	53.5	54.4	1.89
4	58.4	55.2	56.6	56.7	1.86
5	62.1	60.3	61.3	61.2	1.05
7	70.3	67.0	69.7	69.0	1.92
10	76.2	75.4	79.2	76.9	2.21
15	80.3	77.7	82.3	80.1	2.67
20	79.2	77.5	82.5	79.7	2.90
30	79.2	77.7	83.1	80.0	3.14

**Fig. 1** Conversion of Al vs. leaching time

ated products appeared at 830°C for residue obtained from kinetic examination in the first minutes of leaching and at 850°C for ones obtained after 15 and 30 minutes. The second and third peaks appeared at 230 and 190°C and at 285 and 270°C, respectively.

The X-ray examinations show that calcium carbonate products have been formed as vaterite, aragonite and calcite modification of CaCO_3 . The tetracalcium aluminate carbonate 12-hydrate ($\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 12\text{H}_2\text{O}$) was also detected

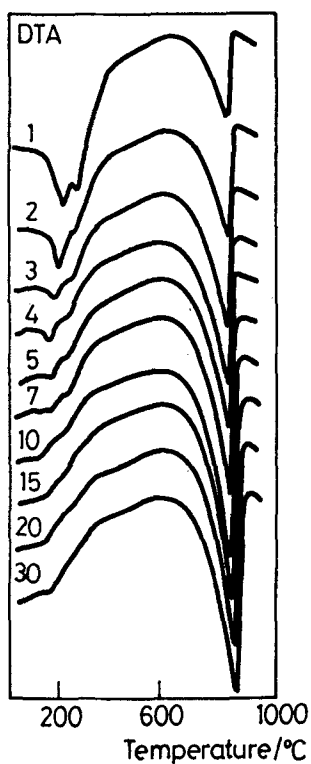


Fig. 2 DTA curves (Paulik & Paulik) from leaching of Al

[7, 8]. Moreover, remained $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ was notable on X-ray diffractograms. There were no other calcium aluminate hydrates in these residues. It was verified, that the bulky of vaterite was mainly formed in the beginning stage of leaching, however, the small amount of aragonite also was formed. The $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 12\text{H}_2\text{O}$ was mainly created in the first minutes of leaching as vaterite and practically disappeared after 10 minutes of process run. It explained the conversion differences calculated from solution and residue in the first minutes of leaching because the weight changes between 100 and 650°C was not taken for conversion calculations. Aragonite was only identified in residues obtained during leaching at 60 and 80°C while vaterite and calcite were predominant modifications of CaCO_3 . Calcite was a principal carbonate product in a residue at the end of a leaching process.

The next precise DTA curves made by SETARAM System (Fig. 4) demonstrate the thermal decomposition of residues obtained during leaching of $2\text{CaO}\cdot\text{SiO}_2$, $12\text{CaO}\cdot\text{Al}_2\text{O}_3$, and *SDP* with soda solution. Results show that the addition peaks at 890, 928 and 977°C was appeared while the chief biggest

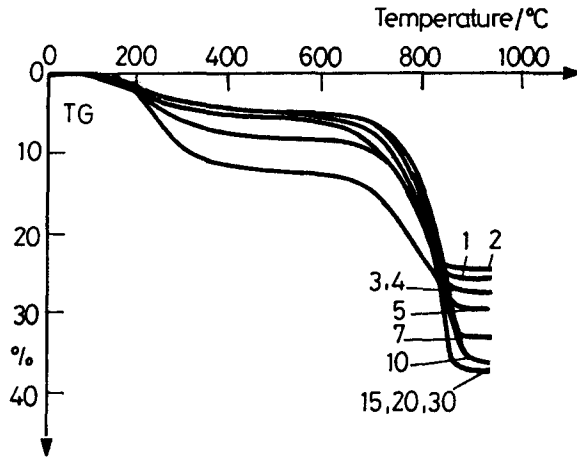


Fig. 3 TG curves (Paulik & Paulik) from leaching of Al

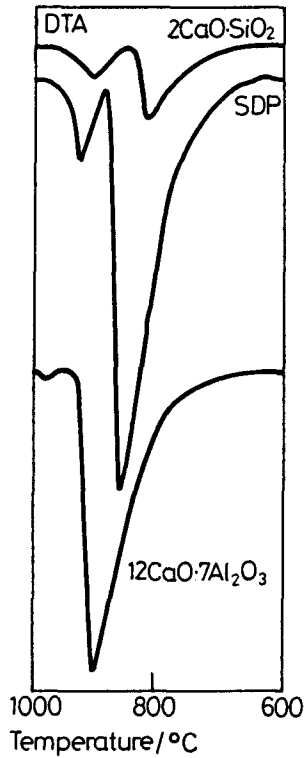


Fig. 4 DTA curves (SETARAM) for determination of a kind of the carbonate products

peaks was exhibited at 818, 862 and 879°C, respectively. The question which carbonate products demonstrate both peaks have been next solved. For this purpose, basing on DTA curves (Fig. 4), residues of mentioned samples were calcinated in an electric furnace at 850 and 910°C, respectively. The X-ray tests revealed that additional peaks at higher temperatures have come only from calcite while ones at lower temperature have come from aragonite and vaterite. Moreover, it was ascertained that calcium orthosilicate ($2\text{CaO}\cdot\text{SiO}_2$) produced aragonite and calcite while calcium aluminate produced the mixture of vaterite, aragonite and calcite.

That discovered rule was very useful for an explanation of the kinetic mechanism of Al leaching.

Conclusions

Results of an experimental study presented and discussed in the present paper led to formulate the following concluding remarks:

- The DTA analysis can be used for the estimations of the conversion of Al in the leaching kinetic tests with 95% of confidence level.
- The DTA analysis was useful for the verification of a kind of carbonate products generated in Al leaching from calcium aluminates and *SDP*.
- Owing to DTA was discovered that in Al leaching in the solid-liquid system calcium orthosilicate produced aragonite and calcite while calcium aluminate produced mixture of vaterite, aragonite and calcite.
- Owing to DTA was also detected that tetracalcium aluminate carbonate 12-hydrate ($\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 12\text{H}_2\text{O}$) exists only in the first minutes of leaching process.

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Zusammenfassung — Komplexe Thermoanalyse wurde bei der Untersuchung der Karbonat-Reaktionsprodukte im Rückstand nach einem Auslaugen aus Calciumaluminat $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ und SDP angewendet. Die Umsetzung von Al wurde auf der Grundlage des aus den kinetischen Untersuchungen stammenden Al-Gehaltes in Lösung als auch im Rückstand berechnet. Die dritte Methode zur Messung der Umsetzung von Al wurde dargelegt und diskutiert. Die Ergebnisse zeigen, daß die vorgeschlagene Methode zur Schätzung der Konversionsrate mit einer statistischen Sicherheit von 95% als auch zur Detektion von Karbonatprodukten benutzt werden kann und daß sie außerdem für die Interpretation des neuen Weges für den kinetischen Mechanismus des Auslaugungsprozesses geeignet ist.