10TH INTERNATIONAL ALUMINA QUALITY WORKSHOP

19 – 23 APRIL 2015 • PERTH • WESTERN AUSTRALIA

Conference Proceedings

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FOREWORD

AQW Inc and the Local Organising Committee welcome you to the 10th International Alumina Quality Workshop, 19-24 April 2015 in Perth, Western Australia.

The Alumina Quality Workshop began in 1988 as a forum to bring the world's alumina producers and their customers together to exchange ideas and information around a common goal of improved product quality. Over time, the workshop has evolved into a major international symposium, incorporating all aspects of the production of alumina from bauxite, of which alumina quality remains an important aspect. The AQW symposia continue to be held in Australia at an interval of three years.

We thank everyone who has participated in the conference and acknowledge the tireless efforts of all of those involved in the organisation, including the team at EECW.

We thank all of our generous sponsors and exhibitors who demonstrate their strength within our industry through their support, making this important event possible.

The organising committee would like to thank all of the authors for their contributions, which form the heart of the workshop. We especially thank the contributors from overseas who have travelled to Australia to present their papers.

We gratefully acknowledge the enormous effort of the technical review panel for reviewing the large number of submitted abstracts and papers. All of your effort is very much acknowledged and appreciated and without your input there could not be a conference.

The theme of this year's conference "Innovation: Refining Our Future" highlights the importance of innovation for not just surviving but for excelling during many years of challenging global conditions. Even amidst a global financial crisis and streamlined operations exciting advancements are constantly taking place.

It's true that sharing much of the international alumina industry development and research is restricted by intellectual property constraints. Nonetheless there are still many opportunities to share knowledge. Innovations that improve integration with the environment (such as residue and mine rehabilitation) are obviously worth sharing. Innovations in analysis and engineering can benefit the industry as a whole by improving efficiency and reducing waste. Collaborative strategic research and technical investigations support the future needs and betterment of the alumina refining and smelting industries as a whole.

These proceedings thus represent the "tip of the iceberg of knowledge" that resides within our industry. They form an excellent starting point to stimulate discussion, collaboration and further innovative both now and for years to come.

In addition to these proceedings, we trust that AQW delegates find ample opportunity for lasting value from the conference through several days of networking, personal interactions and discussions with old friends and new colleagues.

We anticipate you will benefit from the AQW and sincerely hope you find it very worthwhile.

Technical Committee

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COMPREHENSIVE STUDY ON THE DISSOLVED CA(OH)2 IN STRONGLY ALKALINE SOLUTIONS

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ABSTRACT

In order to reveal the possible formation of $Ca(OH)_{2(aq)}$ solution species, NaOH solutions saturated with solid calcium oxide were prepared in the concentration ranges of 0–1 M for ICP-OES measurements (5–75 °C) and 0–4 M NaOH for precipitation titrations and potentiometric investigations (both at 25 °C). The results of these ICP measurements proved that the observed and calculated data are in good agreement only when Ca^{2+}, $CaOH^+$ and $Ca(OH)_2$ solution species are considered together in the chemical model. The calculated thermodynamic constants at 25 °C are as follows: $L(Ca(OH)_{2(s)}) = 8.8\times10^{-5}$ is the solubility product, while $K(CaOH^+) = 1.5$ and $\beta(Ca(OH)_2) = 4.7$ are the stability products.

The distribution diagram calculated on the basis of these constants shows convincingly that the $Ca(OH)_2$ cannot be omitted above the concentration of ~ 0.2 M NaOH. Moreover, dissolved $Ca(OH)_2$ becomes the most significant species above 2 M base concentration. An important consequence is that the total Ca(II) concentration cannot be decreased below ~ 3×10^{-4} M even at the highest concentrations of the base.

1. INTRODUCTION

The heterogeneous and homogenous equilibrium properties of aqueous solutions saturated with $Ca(OH)_{2(s)}$ have been studied many times for a long time. In spite of these efforts, there are still uncertainties about the existing dissolved species, in addition to the unquestionable Ca^{2+}. It has been known since 1923 (Kolthoff, 1923) that the $CaOH^+$ exists in significant concentration and this complex has been also identified by our research group *via* ICP-OES method (Pallagi et al., 2012). However, there is disagreement in the literature about the presence of the dissolved $Ca(OH)_2$.

The vast majority of the previous publications — included the most cited ones (Bates et al., 1959; Davies and Hoyle, 1951; Guiomar et al., 1998) — did not suppose its existence but a few ones considered its appearance. The aim of this work was to clarify the distribution of the existing Ca(II)-containing species in highly alkaline solutions.

2. EXPERIMENTAL

A series of alkaline samples saturated with $Ca(OH)_{2(s)}$ were prepared and the total amount of calcium ($T_{Ca(II)}$) were determined. The procedure of the sample preparation was the following: 12 carbonate-free alkaline solutions were prepared in the range of $c_{NaOH} = 0–1$ M. CaO was added to the alkaline samples and they were stirred for one day under N_2 atmosphere. The samples then were filtered, acidified to pH ~ 1 value. 0.0100 mM Cu^{2+} was added as internal standard. The $T_{Ca(II)}$ was measured by a Thermo's IRIS Intrepid II ICP-OES spectrometer at the wavelength values of 315.8, 317.9 and 393.3 nm.

The whole procedure was carried out at T = 5.0, 25.0, 50.0 and 75.0 °C and the ionic strength was adjusted to 1 M with sodium chloride.

Additional experiments were performed with regard to the existence of the dissolved $Ca(OH)_2$. The calcium(II) ion forms precipitation with the oxalate ion according to the

$$Ca^{2+}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \rightarrow CaC_2O_{4(s)}$$

reaction equation. Distilled water and solutions containing 1, 2, 3 or 4 M NaOH (ionic strength was adjusted to 4 M) were saturated with $Ca(OH)_{2(s)}$ and then stirred for one day at 25 °C. 5 ml of filtered liquid phase was titrated by 0.1 M sodium oxalate. (In the case of distilled water, the Ca(II) containing saturated liquid phase was diluted to 0.55/100 ratio before the titration resulting about 0.001 M total Ca(II) concentration.) The precipitation was followed by recording the absorbance in the 400–700 nm wavelength range with a Shimadzu UV-1650 PC UV-Vis spectrophotometer.

Potentiometric determinations were also performed at 25 °C. The preparation process was the same as for the precipitation titrations. 10 ml of filtered liquid phase was diluted to 10/25 ratio (resulting 1.6 M ionic strength). Each sample was acidified to pH ~ 6 value. $T_{Ca(II)}$ was measured using a Metrohm Titrando 888 automatic titration instrument and a Metrohm-type, combined Ca(II) ion selective electrode (Ca-ISE).

3. RESULTS AND DISCUSSION

3.1 Definitions

[X] is the equilibrium concentration of species X in saturated solutions;

T_X is the total concentration of species X in saturated solutions;

c_{NaOH} is the analytical concentration of the added hydroxide;

$L = [Ca^{2+}][OH^-]^2$ is the solubility product of $Ca(OH)_{2(s)}$.

$K = \dfrac{[CaOH^+]}{[Ca^{2+}][OH^-]}$ is the stability constant of $CaOH^+$;

$\beta = \dfrac{[Ca(OH)_2]}{[Ca^{2+}][OH^-]^2}$ is the stability product of $Ca(OH)_{2(aq)}$.

$Ca(OH)_{2(s)}$ means the solid precipitation and $Ca(OH)_2$ means the species in the aqueous phase in all cases.

3.2 Mathematical Relations

The function $T_{Ca(II)}$ should be determined as a function of c_{NaOH}. Considering the definitions, for the total concentration of Ca(II) ions, the following equations can be written:

$$T_{Ca(II)} = [Ca^{2+}] + [CaOH^+] + [Ca(OH)_2] \qquad (1)$$

$$T_{Ca(II)} = L\left(\frac{1}{[OH^-]^2} + \frac{K}{[OH^-]} + \beta\right) \qquad (2)$$

For expressing T_{OH}, the relations are the following:

$$T_{OH} = [OH^-] + [CaOH^+] + 2[Ca(OH)_2] \qquad (3)$$

$$T_{OH} = [OH^-] + \frac{KL}{[OH^-]} + 2\beta L \qquad (4)$$

The dissolution of $Ca(OH)_2$ (formed by the hydrolysis of CaO) results in a Ca(II) and two OH^- ions in the aqueous phase, which means:

$$T_{OH} = c_{NaOH} + 2T_{Ca(II)} \qquad (5)$$

From Eqs. (2), (4) and (5) the equilibrium concentration of the hydroxide ion can be expressed as:

$$[OH^-]^3 - c_{NaOH}[OH^-]^2 - KL[OH^-] = 0 \qquad (6)$$

The chemically relevant, positive root of this formula can be calculated if the values of *K* and *L* are given and the added concentration of NaOH (c_{NaOH}) is known. Then the calculated $[OH^-]$ can be substituted to Eq. (2) so the $T_{Ca(II)}(c_{NaOH})$ function can be determined.

3.3 Evaluation of ICP data

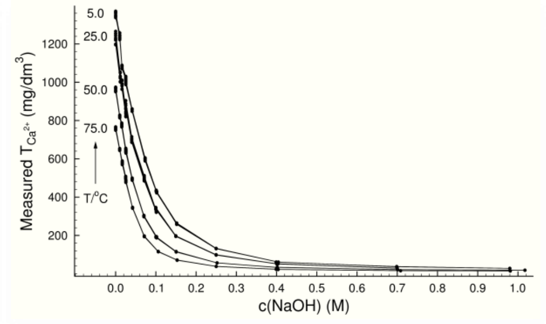

Figure 1. The observed $T_{Ca(II)}$ values acquired by ICP-OES as a function of the added NaOH concentration. The curve consisting the lowest values corresponds to 5 °C.

The observed total calcium(II) concentrations were evaluated by non-linear parameter fitting in order to determine the values of *L*, *K* and *β* at the used temperature values. The difference between the experimental and calculated $T_{Ca(II)}$ values were minimized during fitting. All possible combinations of the three equilibrium constants were tried and the calculations were strictly proved that the dissolved $Ca(OH)_2(aq)$ has significant contribution to the total calcium(II) concentration, it is even more important than $CaOH^+$. It means that both

$$Ca(H_2O)_x^{2+} + OH^- \leftrightarrow CaOH(H_2O)_{x-1}^{+} + H_2O$$

$$Ca(H_2O)_x^{2+} + 2OH^- \leftrightarrow Ca(OH)_2(H_2O)_{x-2}^{2+} + 2H_2O$$

equilibria are necessary to be included in the chemical model to interpret the measured values. Figure 2 illustrates the final result of these calculations at 25 °C while Table 1 gives the determined numerical values of the equilibrium constants.

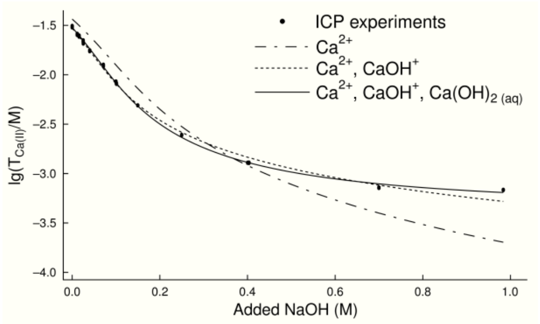

Figure 2. The final result of the non-linear parameter fitting (at 25 °C), when only Ca^{2+} (dash-dotted line), Ca^{2+} and $CaOH^+$ (dotted line), Ca^{2+}, $CaOH^+$ and $Ca(OH)_2$ (solid line) are taken into account.

It can be seen, that assuming only the Ca^{2+} is unsatisfactory still at very low NaOH concentrations. Fitting Ca^{2+} and $CaOH^+$ (according to the previous models) is sufficient only to ~ 0.2 M NaOH. However, the chemical model containing Ca^{2+}, $CaOH^+$ and also $Ca(OH)_2$ can reproduce the experimental values. Another surprising result is that the decrease of $T_{Ca(II)}$ slows down, which is caused by the growing hydroxide concentration. From the measurements at different temperatures the enthalpy and entropy of the corresponding reactions could be determined according to the Van't Hoff equation. These thermodynamic parameters can be found in Table 1.

Table 1. The calculated thermodynamic parameters at different temperatures.

T/°C	*L*	*K*	*β*
5	$(1{,}3\pm0{,}02)\cdot10^{-4}$	1,2±0,1	3,2±0,1
25	$(8{,}8\pm0{,}2)\cdot10^{-5}$	1,5±0,1	4,7±0,1
50	$(4{,}14\pm0{,}07)\cdot10^{-5}$	2,7±0,2	7,2±0,1
75	$(2{,}38\pm0{,}04)\cdot10^{-5}$	3,0±0,1	11,1±0,1
ΔH/kJ·mol^{-1}	–20±2	12±2	14,3±0,4
ΔS/kJ·(mol·K)$^{-1}$	+146±5	43±6	61±1

Figure 3 shows the distribution diagram of the species and the total calcium(II) concentration dependence on the equilibrium hydroxide concentration at 25 °C.

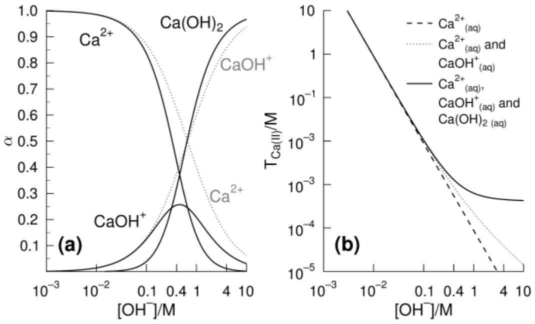

Figure 3. Distribution diagram of the species (a) and total calcium concentration (b) as a function of $[OH^-]$ at 25 °C. Dotted-grayed lines represent the model when $Ca(OH)_2$ is omitted. Dashed line on part (b) means when only Ca^{2+} is taken into account.

From Figure 3a, it can readily be seen that in highly alkaline solutions, calcium(II) ions are present as dissolved $Ca(OH)_2$ rather than either Ca^{2+} or $CaOH^+$. It is also remarkable, that the total concentration of the dissolved Ca(II) cannot be lowered below ~ 0.0003 M by growing the concentration of NaOH (Figure 3b). Smaller, but also minimum values for $T_{Ca(II)}$ could be expected at higher temperatures.

3.4 Precipitation titrations

The previous results (from ICP-OES measurements) indicate that $T_{Ca(II)}$ reaches a minimum value at higher hydroxide concentrations. If the solutions to be titrated would contain different total concentration of Ca(II) then the precipitation would start at different volume of the titrant, and there would be various amount of the solid phase resulting different values in the observed absorbance.

Figure 4 shows the primary data obtained from the spectrophotometric titrations. It can be seen from the figure that without adding NaOH (it is the solution containing only 4 M NaCl), the shape of the titration curve is very different, indicating the higher total concentration of calcium(II). At higher NaOH concentrations (from 1 to 4 M) the maximum mean absorbance appears at the same volume of the titrant, consequently the total calcium(II) concentration is approximately the same in each sample including added hydroxide.

These facts also support that the $Ca(OH)_2$ is the main species in alkaline solutions where the hydroxide concentration is larger than 1.0 M.

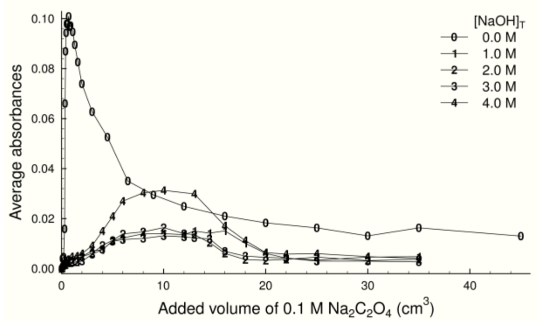

Figure 4. The average of the measured absorbances in the wavelength range of 400–700 nm when saturated calcium(II) solutions were titrated with oxalate solution. The number symbols mean the added hydroxide concentration of the saturated solutions.

3.4 Potentiometric measurements

According to the conception in case of precipitation titrations, if $T_{Ca(II)}$ would become constant at higher hydroxide concentrations, the measured potentials are expected to be identical.

Before the measurements, the ion-selective electrode was calibrated at 25 °C and 1.6 M ionic strength in the concentration range of 0.0001–0.1 M. The slope and the intercept were 28.13 ± 0.06 mV and 100.67 ± 0.07 mV, respectively. The ideal, Nernstian value for the slope is 29.56 mV. This difference between the theoretical and measured value is acceptable, considering the sensitivity of ion-selective electrodes for the changes of ionic strength.

Table 2 contains the measured potentials and the calculated $T_{Ca(II)}$ concentrations.

Table 2. Measured potentials using a Ca(II) ion-selective electrode and the calculated total Ca(II) concentrations at 25 °C

c_{NaOH}/M	E/mV	$T_{Ca(II)}$/M
0	–155.45	0.027
1	–205.45	0.00027
2	–208.60	0.00018
3	–205.52	0.00027
4	–203.77	0.00034

From potentiometric measurements two important facts can be derived. When there is no added NaOH, the value of $T_{Ca(II)}$ is in good agreement with the one that can be calculated from the solubility product according to the formula (under these circumstances, $T_{Ca(II)}$ is approximately equal to $[Ca^{2+}]$):

$$T_{Ca(II)} \approx [Ca^{2+}] = \sqrt[3]{\frac{L}{4}} \qquad (7)$$

In case of samples which contained 1–4 M NaOH, the $T_{Ca(II)}$ values vary between the $(1.8–3.4)\cdot 10^{-4}$ M range. This difference is insignificant comparing to the value valid at 0 M added NaOH. It proves that the total concentration of Ca(II) changes only to a small extent with the increasing concentration of sodium hydroxide, reaching a limited value.

4. CONCLUSIONS

Our experiments proved that the dissolved calcium hydroxide cannot be omitted from the speciation of alkaline calcium(II) solutions. In highly alkaline solutions, dissolved $Ca(OH)_2$ is formed rather than either Ca^{2+} or $CaOH^+$. The total concentration of the dissolved Ca(II) cannot be decreased below 0.0003 M at room temperature. This limiting concentration decreases with the increasing temperature, but some constant calcium concentration is expected even at the highest (industrially relevant) temperatures, too. These facts may influence laboratory procedures, *e.g.*, preparing carbonate-free solutions using $Ca(OH)_2$. Moreover, the presence of $Ca(OH)_2$ must be taken into consideration in processes of industrial importance.

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