

Reaction of $\text{Ca}(\text{OH})_2$ with HCl in the presence of water vapour at low temperatures

M. Bausach^{a,b,*}, G. Krammer^a, F. Cunill^b

^a *Institut für Apparatebau, Mechanische Verfahrenstechnik und Feuerungstechnik, Technische Universität Graz, Graz, Austria*

^b *Departament d'Enginyeria Química i Metal·lúrgia, Universitat de Barcelona, Barcelona, Spain*

Received 12 January 2004; received in revised form 2 April 2004; accepted 14 April 2004

Available online 21 July 2004

Abstract

The final products of the reaction between HCl and $\text{Ca}(\text{OH})_2$ can be $\text{Ca}(\text{OH})\text{Cl}$, CaCl_2 , or both simultaneously depending on the temperature, HCl concentration and reaction time. A possible mechanistic pathway consistent with the experimental results concerns two consecutive reactions: The formation of $\text{Ca}(\text{OH})\text{Cl}$ and the final formation of CaCl_2 from the reaction of $\text{Ca}(\text{OH})\text{Cl}$ with HCl. However, the second reaction might take place only, when $\text{Ca}(\text{OH})_2$ is missing. The amount of water retained by the solid during the reaction between HCl and $\text{Ca}(\text{OH})_2$ reaction is determined at 120 °C and 18% relative humidity employing a thermogravimetric analyser. The amount of water retained is a measure for the tendency of the solid to agglomerate. The stability of the $\text{Ca}(\text{OH})\text{Cl}$ at ambient conditions is studied and found to be good. © 2004 Elsevier B.V. All rights reserved.

Keywords: Thermogravimetric analyser; In-duct dry sorbent injection; Desulfurisation; Hydrogen chloride

1. Introduction

In-duct dry sorbent injection technologies (IDS) have been traditionally applied for the desulfurisation of flue gases emitted by coal-fired furnaces. Their use is currently extended towards the retention of other gaseous acidic pollutants such as hydrogen chloride (HCl) formed during, e.g., waste incineration, where chlorinated compounds are burned.

IDS technologies are usually based on the injection of an alkali sorbent namely $\text{Ca}(\text{OH})_2$ in the waste flue gas ducts. The dechlorination takes place industrially in the temperature range of 70–200 °C. Calcium hydroxide particles are conveyed by the gases until the solid is withdrawn by a particulate collector [1].

During combustion also an appreciable amount of water vapour is formed which is also present in the flue gas. During the operation of IDS processes acid gas removal is enhanced when the water content is high, which can be achieved by spray cooling. But a high water vapour content can also

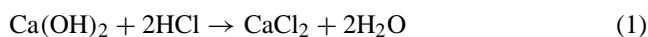
involve negative consequences on plant operation: Wetted solids tend to agglomerate more easily, causing problems of solid deposition [2]. Moreover, the deposition of solid products in landfills can be more difficult, due to the problems of solubilisation. Therefore the determination of both the kind of reaction products and the amount of retained water during the reaction in the presence of water vapour are of great interest in the application of IDS technologies. Especially the amount of freely movable liquid is a measure for the tendency of particles to agglomerate.

As reported in many studies at laboratory scale, increasing temperature (up to 800 K) and higher relative humidity augment the reaction of Ca adsorbents with HCl [3–9]. Based on the results of an integral fixed bed reactor [5,6], working at low temperature in the presence of water vapour, claimed that at HCl concentrations up to 1000 ppm the rate of absorption is first order with respect to the HCl concentration, except at early reaction times where Chisholm and Rochelle [6] proposed a pseudo-second-order reaction.

Only little information is available in literature dealing with the identification of final products and mechanistic pathways [4,7,10]. Most of the studies reported in literature [3,5,8] assume that calcium chloride, CaCl_2 , or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is the final product of the reaction between hydrogen chloride

* Corresponding author. Tel.: +34-934021312; fax: +34-934021291.
E-mail address: mbausach@ub.edu (M. Bausach).

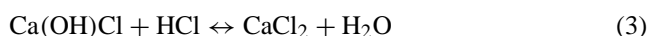
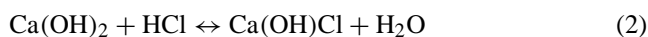
(HCl) and Ca-based, according to the following equation:



Millikan [11] already stated this reaction working with aqueous systems. Weinell et al. [3], Fonseca et al. [5], and Chisholm and Rochelle [6], working at temperatures between 50 and 120 °C and in the presence of water vapour, reported a final conversion at a ratio of 1–2 based on Cl/Ca indicating that at least a fraction of the product consists of CaCl₂. Karlsson et al. [8] reported that the final conversion is reached at a ratio close to 1.1.

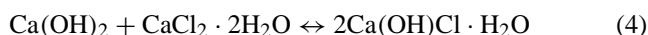
Daoudi and Walters [7] found that CaCl₂ was the only final product when calcined CaCO₃, i.e. CaO was employed at temperatures between 310 and 670 °C. They also verified that the maximum weight increase corresponded to full conversion of CaO to CaCl₂. In contrary, Jozewicz and Gullett [4] detected both CaCl₂·2H₂O and Ca(OH)Cl as chlorinated products after the reaction of Ca(OH)₂ with HCl for 1 min at 500 °C, but they only found Ca(OH)Cl at 200 °C, which was also reported by Allal et al. [10] for a residence time of 0.5 s at 250 °C. (Both groups were working at dry conditions.)

The comparison between CaCl₂ and Ca(OH)Cl indicates that both compounds are formed by the substitution of one and two hydroxyl groups in Ca(OH)₂, respectively. This fact suggests that reaction (1) could take place via the intermediate Ca(OH)Cl, as was already pointed out by Jozewicz and Gullett [4] in the following way:



Reaction (3) is also reported by Gmelin [12].

Besides, XRD analysis of mixtures of Ca(OH)₂ and CaCl₂·2H₂O carried out in Refs. [4,10] reflected the formation of Ca(OH)Cl. The following reaction was proposed:



which was found thermodynamically viable. Allal et al. [10] estimated the free enthalpy of formation of Ca(OH)Cl and evaluated the equilibrium constants of the reactions (1), (2), (3), and (4) in the range from 373 to 1000 K. They concluded that all reactions can occur in the range of temperatures studied.

The stoichiometry of the reaction with respect to chloride in the solid product seems to be undecided though this information is essential when considering the characteristic data of total conversion, i.e. maximum uptake of chloride by the sorbent. Dependent upon the kind of reaction product also the chemical stability is an issue when considering the situation in landfills, where these reaction products are often deposited. Moreover also the amount of freely movable liquid can depend upon the kind of reaction product.

The present work is devoted to describe the reaction behaviour of the system Ca(OH)₂ and HCl in the presence of water vapour at low temperatures. It is especially focused on

the determination of the final products of reaction and their stability, as well as on the evaluation of the amount of HCl retained during the reaction. In addition, both the water adsorbed during the reaction and the remaining water after a drying period is determined. Finally, a mechanistic reactive pathway is proposed.

2. Experimental

Experimental runs were performed to determine the HCl and water retained in the sorbent by means of a thermogravimetric analyser (TGA). HCl was supplied as a gas mixture (HCl/N₂) from a gas cylinder, and water vapour was produced by means of a steam generator that expands liquid water through a sintered metal block. The sample holder and the sample holder chain were made of inconel, which is inert when exposed to HCl.

Some preliminary experiments were done in order to evaluate the most appropriate procedure to perform this study. The results showed that the total weight of a sample was reduced considerably when the sample was dried. It reflected the hygroscopic character of the products formed, so that the variation of total weight during the experiment was associated to two different contributions: The reaction of Ca with HCl and the retained water.

TGA experiments consisted of three consecutive periods which can be seen in Fig. 1. In the first one (about 1500 s) the sample was dried at 120 °C by circulating pure N₂ over it. Afterwards, the required HCl and water were supplied and the reaction started at a constant temperature (120 °C) for a desired reaction time (always shorter than 2000 s). Finally, after the reaction had been terminated, the sample was dried again by circulating pure N₂ over it with the same flow that was employed in the first period, till the weight became constant (about 3 min). The signal of the total weight of the sample was recorded at a rate of 15 s. All experiments were undertaken at 120 °C, 18% relative humidity, 240 ppm of HCl, 3.2 mg of sample, and a total flow of 0.9 l/min stp.

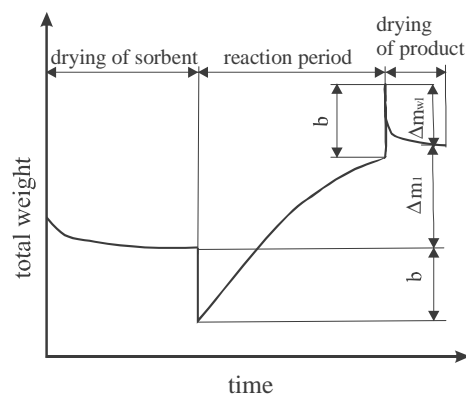


Fig. 1. Schematics of total weight change during TGA experiment—results unaccounted for different buoyancy.

The moisture content in the samples during the reaction can be divided in two parts: one fraction that is easily removed by a short drying period, and another fraction that remains after this period, which is more strongly bound to the solid. The fraction of water that is strongly linked to the crystal is determined by taking the weight difference between the final dry product and the weight of the unreacted sample (indicated as Δm_1 in Fig. 1). This weight difference Δm_1 is the sum of the strongly bound water Δm_{W_s} and the increase due to the uptake of HCl according to reaction (2). The amount of Cl, n_{Cl} , that is reacted with Ca(OH)_2 is determined by standard methods. This gives

$$\Delta m_{W_s} = \Delta m_1 - n_{Cl}(\text{MW}_{\text{Ca(OH)Cl}} - \text{MW}_{\text{Ca(OH)}_2}) \quad (5)$$

where MW denotes the molecular weight, n_{Cl} the moles of Cl in the solid sample and Δm_{W_s} the amount of strongly bound water. The amount of loosely bound water, Δm_{W_l} , can be determined directly from weight decrease during the drying step of the product (see Fig. 1). Since the gas atmosphere is different between the reaction period and the drying periods, also the buoyancy is different. Its contribution is schematically indicated by 'b' in Fig. 1. Because the start of the reaction and the start of the drying period coincides with the change of buoyancy, the respective starting locations are difficult to determine which results in some inaccuracy especially for the drying period which starts at a high rate. The total amount of water that is taken up by the sorbent is given by

$$\Delta m_W = \Delta m_{W_l} + \Delta m_{W_s} \quad (6)$$

The reproducibility of the results was in the range of 8–16% (standard deviation with 95% confident interval), which made a large number of experiments necessary at the same conditions. The low sample weight and critical gas species of H_2O and HCl caused surprisingly large data fluctuations.

The raw material used in this work was a commercially available limestone (Bad Ischler limestone) containing 5% inert and 95% CaCO_3 . A fraction of particles with a diameter range of 50–63 μm was prepared by sieving and it was used to prepare the Ca-based reagent. The preparation included two steps. First, the sample was calcined in the TGA, so that CaO was formed. Afterwards, the sample was cooled and taken out of the TGA. The CaO was dispersed on a surface and it was slowly moistened pouring water droplets on it. This gentle procedure was chosen to prevent particle fragmentation. The conversion towards Ca(OH)_2 was tested by heating a sample in the TGA and it was found to be close to 100%. Depending on the duration of the storage, Ca(OH)_2 picked up some CO_2 from the air to form CaCO_3 . For the experiments two different levels of re-carbonated Ca(OH)_2 were used with 77 and 58% of Ca(OH)_2 , respectively.

As the TGA experiments only provided the total weight, additional analyses were required to determine the actual conversion. Two different standard methods were employed—ion chromatography and chlorine potentiometry—to analyse the amount of Cl^- in a liquid

sample at different conversion. Only some of the samples were analysed chemically with respect to the Cl^- content. Since an excellent correlation was found between the total increasing weight of the sample after the drying period and the amount of Cl^- found in the sample, this correlation was employed to determine the Cl^- content of all other experiments. The structural composition of the final reaction product was identified by X-ray diffraction (XRD). Some chemical analyses of the final product were performed before and after the drying period to find out whether the final drying step would alter the amount of Cl^- retained. For XRD a sample size of more than 1 g was prepared.

In order to evaluate whether TGA experiments are appropriate to do kinetic studies of the reaction between HCl and Ca(OH)_2 , some experiments were carried out changing the amount of sample from 1 to 10 mg. The results (not shown here) showed that both the amount of HCl retained and the reactions rates obtained from this data decreased when the amount of sample was increased. This clearly indicates that the TGA setup used here does not provide differential conditions. Also compaction and channelling might have occurred in the sample. Amounts lower than 1 mg were not checked, because of limits of accuracy of the TGA balance. Appropriate geometries of the sample holder were also tested to eliminate external mass transfer resistance which can, however, not be excluded for the results presented here. Consequently, it is concluded that no accurate kinetic data can be obtained from TGA experiments, at least for the setup chosen.

3. Results and discussion

3.1. Final product and its stability

The results of X-ray diffraction of a reacted sample at 120 °C and 18% of relative humidity are shown in Fig. 2. It can be seen in the XRD pattern (a) that the only product detected was Ca(OH)Cl , which was analysed immediately after the sample was produced. Another sample was prepared at the same reaction conditions, which was analysed 24 h after its production. The XRD pattern that was obtained is also depicted in curve (b) of Fig. 2. Both patterns are basically identical indicating that the solid formed is a stable product at ambient conditions (relative humidity: $66 \pm 10\%$; temperature approximately 20 °C) for at least 24 h.

The presence of Ca(OH)Cl was already found in other studies [4,10]. This reaction product implies a stoichiometric coefficient of at most one based on Ca and Cl which is, however, in contradiction to Refs. [3,5,6,9] which report ratios of Cl/Ca beyond 1. This discrepancy might be solved when considering Ca(OH)Cl as an intermediate product that continues to react with HCl to form CaCl_2 when Ca(OH)_2 is lacking at least locally. Local EDXS analyses of Ca and Cl of cross-sections of single particles clearly show that the ratio of Cl/Ca is locally higher than 1 though at other locations in the particle it is below 1 [13].

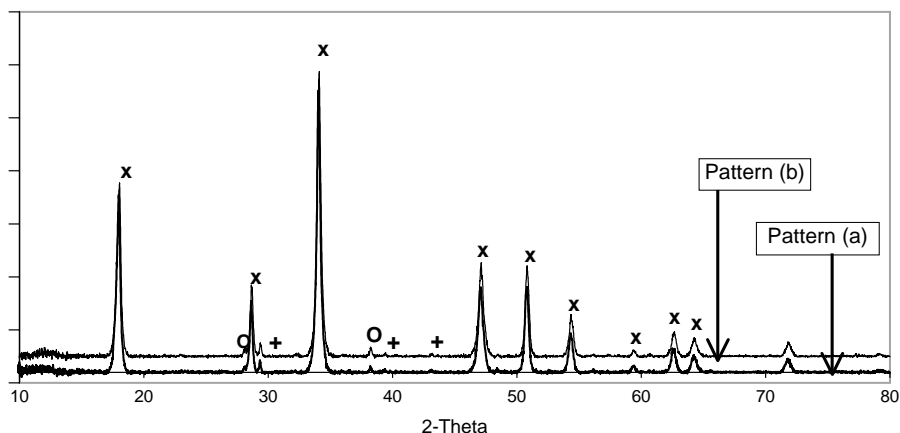


Fig. 2. XRD patterns of a sample from TGA experiment with only Ca(OH)Cl as a product (a) immediately after reaction and (b) after 24 h: (x) Ca(OH)_2 (Portlandite); (+) CaCO_3 (Calcite); (o) Ca(OH)Cl .

In order to confirm the long-term stability of Ca(OH)Cl , a sample of Ca(OH)Cl was left in contact with the atmosphere at room temperature for 8 days before it was analysed by X-ray diffraction. Fig. 3 shows the comparison between the sample that was just prepared (a) and after 8 days (b). Since Ca(OH)Cl is not commercially available, the sample was prepared by mixing chemically grade CaCl_2 with Ca(OH)_2 (20% of CaCl_2 at room temperature in air with moderate humidity). This solid mixture is quickly, i.e. within 10 min, converted to a mixture of Ca(OH)_2 and Ca(OH)Cl according to reaction (4). The XRD patterns show that only Ca(OH)_2 and Ca(OH)Cl and no CaCl_2 is present in the sample. The reaction of CaCl_2 and Ca(OH)_2 seems only to be feasible, if CaCl_2 picks up water from the air to create a liquid phase where the formation of Ca(OH)Cl is occurring quickly. A purely solid–solid reaction seems to be quite unlikely. Moreover, the peaks of Ca(OH)Cl remain unchanged irrespective of the time of exposure confirming the stability of the product.

Finally, the stability of the sample during the drying period of the TGA experiments was checked. The results of the amount of Cl^- found by the solid analyses before and

after the drying period (3 min at 120°C) are approximately the same considering the experimental error, i.e. the amount of HCl that can be driven out during the drying period is negligible. Since no HCl is liberated during this period the reverse reactions of (2) and (3) do not occur, but the possibility that reaction (4), i.e. CaCl_2 forms Ca(OH)Cl during drying cannot be entirely excluded. This is, however, unlikely considering the aforesaid where CaCl_2 is not formed as long as Ca(OH)_2 is present.

3.2. HCl retention

According to the overall reaction equation (2), that is confirmed by XRD analysis, 1 mol of Ca(OH)Cl is formed from the retention of 1 mol of HCl . Fig. 4 shows the transient conversion of Ca(OH)_2 that was determined by chemically analysing the Cl^- content at various reaction times. But it should be taken into account that the TGA experiment was accompanied by external mass transfer limitation. Consequently the reaction rate was lower which in turn can have an influence on the kind of reaction product.

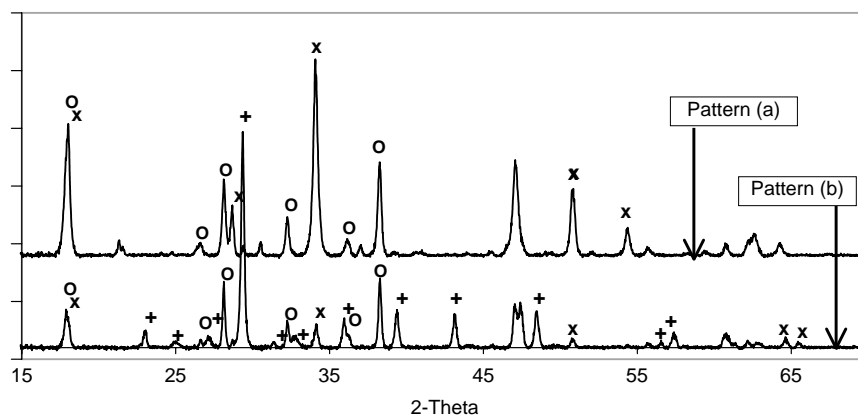


Fig. 3. XRD patterns of a sample prepared by mixing Ca(OH)_2 and chemically grade CaCl_2 at ambient conditions (a) just after preparation and (b) after 8 days: (x) Ca(OH)_2 (Portlandite); (+) CaCO_3 (Calcite); (o) Ca(OH)Cl .

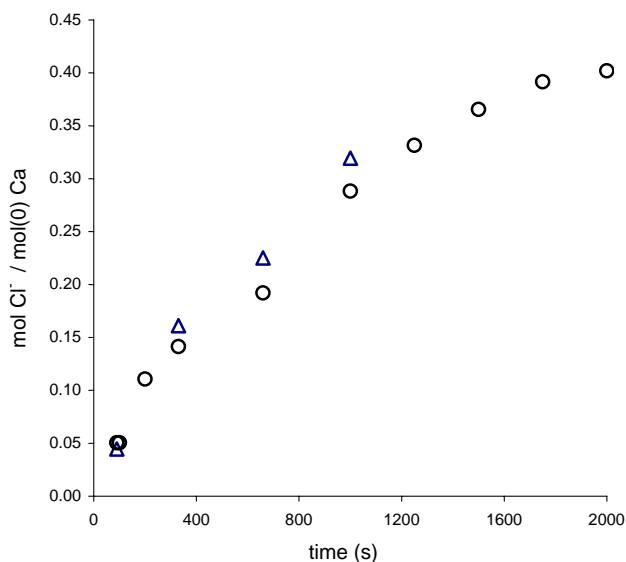


Fig. 4. Transient HCl retention by lime with different Ca(OH)_2 content at a temperature of 120°C , relative humidity of 18% and 240 ppm HCl: (○) 77% Ca(OH)_2 ; (△) 58% Ca(OH)_2 .

The usage of calcium hydroxide re-carbonated to different levels for HCl retention experiments did not show any significant difference, which can also be seen in Fig. 4. For the desulfurisation reaction Klingspor et al. [14] pointed out that the reaction rate is governed by the reaction surface area irrespective whether Ca(OH)_2 or CaCO_3 is present. If this were true also for the HCl removal, the re-carbonation reaction would not cause a significant change of the surface area at least at the low reaction rates present when CO_2 is picked up by Ca(OH)_2 from the air. Of course, also the extent of re-carbonation was low.

The influence of the HCl concentration was studied in the range 150–350 ppm. The results are shown in Fig. 5, indicating that the amount of HCl retained follows a linear

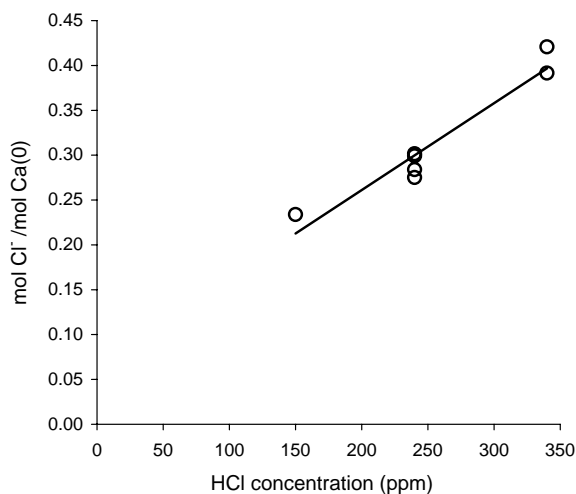


Fig. 5. HCl retention by lime after 1000 s at a temperature of 120°C and a relative humidity of 18%.

trend with respect to the HCl concentration, i.e. first-order reaction, which is in agreement with the results of Chisholm and Rochelle [6].

3.3. Water retention

In Fig. 6 the total amount of H_2O that is taken up during the reaction and the respective fractions are displayed together with their linear trend lines. Both fractions are increasing with increasing conversion with almost the same slope: $0.6 \text{ mol H}_2\text{O/mol Cl}^-$ for strongly bound water and $0.4 \text{ mol H}_2\text{O/mol Cl}^-$ for loosely bound water. The trend lines have a positive value at the intersect with the ordinate, i.e. when no Cl is taken up. This intersection is much higher than one would measure for pure Ca(OH)_2 . This indicates that already a very small amount of Cl alters the surface chemistry considerably to allow a much higher uptake on water. Since the trend line for loosely bound water is increasing with increasing conversion this H_2O uptake cannot only be attributed to an effect of the size of the surface area but also to changing surface adsorption features hence capacity.

In comparison also the moisture content is determined that Ca(OH)Cl , Ca(OH)_2 , and CaCl_2 can pick up when in contact with the atmosphere at room temperature after some days. The samples of commercially available Ca(OH)_2 , and chemically grade CaCl_2 were pure, but the sample of Ca(OH)Cl was prepared by mixing 20% CaCl_2 with Ca(OH)_2 . The amount of water retained by Ca(OH)_2 is practically negligible. But Ca(OH)Cl is obviously hygroscopic (can retain around $2 \text{ mol H}_2\text{O/mol Ca(OH)Cl}$). Finally CaCl_2 , that takes up $9 \text{ mol H}_2\text{O/mol CaCl}_2$, is highly hygroscopic, which is also reported in the literature [15]. These results allow to conclude that if Ca(OH)Cl is formed, problems related to an excess of water in the solid product from an IDS

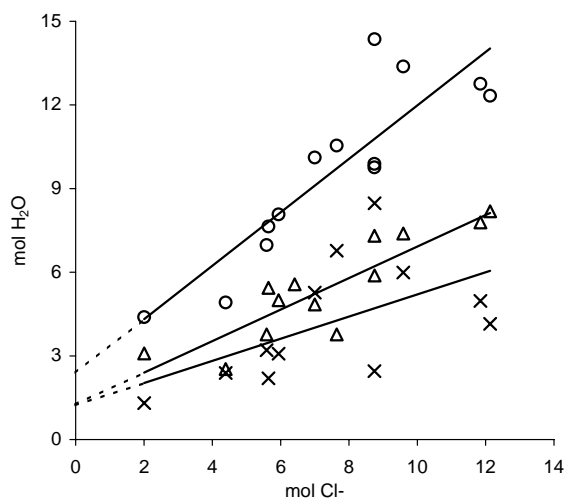


Fig. 6. Water retained at various levels of HCl uptake. The retained water is divided into a loosely bound fraction, i.e. that can be removed during drying at 120°C and a fraction that cannot be removed during this drying procedure: (○) total water uptake (Δm_{W}); (△) strongly bound water (Δm_{W_s}); (×) loosely bound water (Δm_{W_l}).

process are lower compared to those when CaCl_2 is formed as a product.

3.4. Mechanistic pathway

On the premise that Ca(OH)Cl is detected as the only final product of the reaction between HCl and Ca(OH)_2 at low temperatures, a mechanistic pathway can be proposed based on the elementary reaction between Ca(OH)_2 and HCl (reaction 2). But just allowing reaction (2) would be inconsistent with the results reported in Refs. [3,5,6,9] that shows stoichiometric ratios of Cl/Ca beyond 1 or which claim a reaction product of CaCl_2 . This gives rise to the hypothesis that CaCl_2 is formed by the elementary reaction (reaction (1)), and a consecutive reaction of CaCl_2 with the remaining Ca(OH)_2 (reaction (4)), to finally generate Ca(OH)Cl . According to Allal et al. [10] all these reactions are possible from the thermodynamic perspective, though the reaction tends to be irreversible at low temperature flue gas cleaning process conditions. This pathway where CaCl_2 is considered to be an intermediate product requires that the formation of CaCl_2 is the rate determining step, because no CaCl_2 was formed at, however, very short reaction times [4,10]. The fact that at longer reaction times only CaCl_2 was formed [7] would require the possibility of a reverse reaction (4) which is however thermodynamically not favoured.

Of course, also two consecutive reactions (2) and (3) can represent the reaction schema. But making the premise that Ca(OH)Cl is the only product requires the constraint that reaction (3) will only occur, if Ca(OH)_2 is lacking, at least locally. Such a situation will intrinsically be present, if all the available Ca(OH)_2 is used to form Ca(OH)Cl , which can explain the results presented in Refs. [3,6]. Under the hypothesis that during the reaction a product layer is formed in the particle which proceeds towards the centre, Ca(OH)_2 can be missing locally when transport is reaction limiting. This will occur preferentially at higher reaction rates caused, e.g., by higher temperatures or higher HCl concentrations. This schema would allow to also explain the results from Refs. [4,7]. Furthermore from the kinetical point of view bimolecular reactions involved in this mechanistic pathway are usually more favoured than the three-molecular reactions.

4. Conclusions

Based on the results obtained in this work, the reaction between HCl and Ca(OH)_2 at low temperature forms most likely Ca(OH)Cl . But under certain conditions (not tested in this paper) the final product of the reaction can be CaCl_2 . A possible mechanistic pathway consistent with these experimental results and various seemingly diverse results from literature concerns two consecutive reactions: (1) the formation of Ca(OH)Cl (reaction (2)) and (2) the final formation of CaCl_2 from the reaction of Ca(OH)Cl with HCl (reaction (3)). However, to explain all the results obtained at differ-

ent experimental conditions, the second reaction is under the constraint that it only takes place, if Ca(OH)_2 is lacking, at least locally. This situation is favoured at high temperature or at high HCl concentrations, as well as at high conversions.

The reaction product Ca(OH)Cl is found to be hygroscopic but to a much lower extent compared with CaCl_2 . Therefore, in order to reduce the probability of uncontrolled agglomeration that could cause operational problems during IDS processes, Ca(OH)Cl is to be favoured as a reaction product over CaCl_2 though the maximum theoretical conversion is only 50%. Moreover CaCl_2 has deliquescent properties which does not make it suitable for deposition in landfills or as a construction material. In contrary, Ca(OH)Cl was found to be a stable product in contact with the atmosphere.

Future tests under kinetically controlled conditions must be carried out to derive kinetic data. But preliminary tests already indicate that the reaction is first order with respect to HCl .

Acknowledgements

The authors wish to thank the Institute of Electron Microscopy, Graz, the Austrian Energy and Environment AG, and the Verbund Umwelttechnik GmbH namely Mr. Pagger and Mrs. Fraissler for their valuable contributions. Also the experimental support provided by Mr. Koch and Mr. Sacher is gratefully acknowledged.

References

- [1] H.N. Soud, FGD Installations on Coal-fired Plants, 2nd ed., IEA Coal Research, London, 1994.
- [2] N. De Nevers, Ingeniería de control de la contaminación del aire, McGraw Hill Interamericana Editores, S.A. de C.V., Méjico, 1998 (ISBN 0-07-061397-4).
- [3] C.E. Weinell, P.I. Jensen, K. Dam-Johansen, H. Livbjerg, Hydrogen chloride reaction with lime and limestone: kinetics and sorption capacity, *Ind. Eng. Chem. Res.* 31 (1992) 164–171.
- [4] W. Jozewicz, B.K. Gullett, Reaction mechanisms of dry Ca-based sorbents with gaseous HCl , *Ind. Eng. Chem. Res.* 34 (1995) 607–612.
- [5] A.M. Fonseca, J.J. Órfão, R.L. Salcedo, Kinetic modeling of the reaction of HCl and solid lime at low temperatures, *Ind. Eng. Chem. Res.* 37 (1998) 4570–4576.
- [6] P.N. Chisholm, G.T. Rochelle, Dry absorption of HCl and SO_2 with hydrated lime from humidified flue gas, *Ind. Eng. Chem. Res.* 38 (1999) 4068–4080.
- [7] M. Daoudi, J.K. Walters, A thermogravimetric study of the reaction of hydrogen chloride gas with calcined limestone: determination of kinetic parameters, *Chem. Eng. J.* 47 (1991) 1–9.
- [8] H.T. Karlsson, J. Klingspor, I. Bjerle, Adsorption of hydrochloric acid on solid slaked lime for flue gas clean up, *J. Air Pollut. Control Assoc.* 31 (11) (1981) 1177–1180.
- [9] G. Mura, A. Lallai, Reaction kinetics of gas hydrogen chloride and limestone, *Chem. Eng. Sci.* 49 (1994) 4491–4500.
- [10] K.M. Allal, J.C. Dolignier, G. Martin, Reaction mechanism of calcium hydroxide with gaseous hydrogen chloride, *Revue de l'institut français du pétrole* 53 (6) (1998) 871–880.
- [11] J. Millikan, Die Oxyhaloide der alkalischen Erden, *Z. Phys. Ch.* 92 (1918) 496.

- [12] Gmelins Handbuch der Anorganischen Chemie, vol. 28, Verlag Chemie, Berlin, 1956–1957.
- [13] M. Koch, Reaktionsmechanismen von sauren Gasen mit Kalziumhydroxid, Diploma Thesis, University of Technology, Graz, Austria, 2004.
- [14] J. Klingspor, A. Strömberg, H. Karlsson, I. Bjerle, Similarities between lime and limestone in wet-dry scrubbing, *Chem. Eng. Process.* 18 (1984) 239.
- [15] Ullmann's Encyclopaedia of Industrial Chemistry, 6th ed., Wiley-VCH, Weinheim, 2003 (ISBN 3-527-30585-5).