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REACTION MECHANISM OF CALCIUM HYDROXIDE WITH GASEOUS HYDROGEN CHLORIDE

K. M. ALLAL, J.-C. DOLIGNIER and G. MARTIN

Institut français du pétrole[1]

MÉCANISME DE RÉACTION DE L'HYDROXYDE DE CALCIUM AVEC DE L'ACIDE CHLORHYDRIQUE GAZEUX

La diminution de la teneur en gaz acides dans les effluents provenant des unités de combustion ou d'incinération peut être accomplie en faisant réagir ces gaz polluants avec des absorbants alcalins tels que l'oxyde ou l'hydroxyde de calcium. Dans cet article, à l'étude thermodynamique des différentes réactions mises en jeu durant le processus de déchloruration, s'ajoute une étude expérimentale menant à l'identification des produits finaux en utilisant la diffraction X, la microscopie électronique ainsi que la thermogravimétrie. À l'issue de cette étude, il a été montré que la réaction de $Ca(OH)_2$ avec HCl entraîne la formation non seulement de $CaCl_2$ mais aussi CaClOH.

REACTION MECHANISM OF CALCIUM HYDROXIDE WITH GASEOUS HYDROGEN CHLORIDE

The reduction of acid gas content in combustion or incineration flue gases can be carried out by reaction with dry, fine alkaline sorbents such as calcium oxide or calcium hydroxide. In the present work, in addition to the thermodynamic study of the different reactions involved in the dechlorination process, an experimental study to identify the reaction products by means of X-ray diffraction, electron microscopy and thermogravimetry has been carried out. It has been shown that the reaction of hydrochloric acid with hydrated lime leads to the formation of not only calcium chloride but calcium hydroxichloride.

MECANISMO DE REACCIÓN DEL HIDRÓXIDO DE CALCIO CON EL ÁCIDO CLORHÍDRICO GASEOSO

La disminución de la concentración de gases ácidos en los efluentes procedentes de las unidades de combustión o de incineración, se puede conseguir haciendo reaccionar estos gases contaminantes con adsorbentes alcalinos, como,por ejemplo, el óxido o el hidróxido de calcio. En el presente artículo, y como complemento del estudio termodinámico de las diversas reacciones que intervienen durante los procesos de descloruración, se ha emprendido un estudio experimental destinado a identificar los productos finales, utilizando para tal menester la difracción X, la microscopia electrónica así como la termogravimetría. Al término de este estudio, se ha podido demostrar que la reacción de $Ca(OH)_2$ con HCl da lugar a la formación, no sólo de $CaCl_2$ sino también de CaClOH.

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INTRODUCTION

Incineration is practiced nowadays as an alternative to land filling of municipal solid wastes. In spite of the obvious advantages, such as significant volume reduction and the potential for energy recovery from waste, wide application of this technology has been restricted because of the public concern over harmful air emissions from the process, namely acid gases. Among the most important is hydrochloric acid formed during the incineration of PVC, paper and the NaCl content in domestic wastes. A purification step prior to the release of the flue gases into the atmosphere is therefore necessary. One way to reduce the HCl content is by reaction with dry, fine alkaline sorbents such as calcium hydroxide [1 and 2]. Such a reaction is of great interest for the control of acid gas emissions.

Studies on the removal of HCl by hydrated lime have not been reported to the same extend as sulfur dioxide removal. Also, the kinetic and the plant performance data on hydrogen chloride removal from operating processes seem to be scarce and incomplete.

In some previous works [3, 4, 5] calcium chloride was identified as being the only reaction product from the following reaction:

$$Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O \qquad (1)$$

If one assumes that the reaction takes place according to Reaction (1), then the result is a product molar ratio of calcium to chlorine Ca/Cl equal to 0.5 in case of complete conversion. Hence any reaction product having a Ca/Cl molar ratio of more than 0.5 means either incomplete sorbent utilization or the formation of a compound with a Ca/Cl molar ratio greater than 0.5. If this is the case, then complete sorbent utilization could happen although the Ca/Cl ratio is greater than 0.5 and Reaction (1) would consequently not be an appropriate description of the reaction mechanism.

It seems that the reaction mechanism is more complex. Gullet *et al.* [6] were able to identify the presence of other solid phases in the reaction products, in particular calcium hydroxichloride. This compound was in fact detected as early as 1990 by Kosnyrev [7] when mixing calcium hydroxide with calcium chloride. Jozewicz *et al.* [8] have since shown that calcium hydroxide can react with hydrogen chloride, and have finally proposed the following reaction mechanism:

$$Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2.2\ H_2O \qquad (1)$$

$$Ca(OH)_2 + HCl \rightarrow CaClOH.H_2O \qquad (2)$$

$$Ca(OH)_2 + CaCl_2.2\ H_2O \rightarrow 2\ CaClOH.2\ H_2O \qquad (3)$$

$$CaClOH.H_2O + HCl \rightarrow CaCl_2.2\ H_2O \qquad (4)$$

Reactions (1) and (2) show that CaClOH might be formed following contact with HCl.

It is important to identify the reaction products in order accurately to determine the sorbent utilization during the dechlorination process.

In the present work, in addition to the thermodynamic study of the reactions involving calcium hydroxichloride, an experimental study to identify the reaction products by means of X-ray diffraction, electron microscopy and thermogravimetry has been carried out.

1 THERMODYNAMIC STUDY

It would be interesting to study the reactions cited above that are involved in the dechlorination process in order to determine whether they could theoretically take place.

Since the thermodynamic data of CaClOH are not available in the literature, Allal *et al.* [9] have proposed a method to evaluate them. This technique, based on the same approach initially developed by Kosnyrev [10], leads to a linear relation between the Gibbs energy and the enthalpy of formation of the earth alkali hydroxichloride, expressed as:

$$\Delta G^T_{f,Me\mathrm{ClOH}} = a(T)\Delta H^T_{f,Me\mathrm{ClOH}} + b(T) \qquad (5)$$

The values of *a* and *b* of the earth alkali hydroxichloride have been determined by Allal *et al.* [9]. To validate and strengthen their technique, the predicted values of the free enthalpy of formation of MgClOH have been compared to those mentioned in the literature. Table 1 shows that the calculated values are in good agreement with those reported in Jannaf's tables.

The effect of the temperature on the equilibrium constant K of Reactions (1), (2), (3) and (4) is represented in Figure 1. It can be seen first, as far as the thermodynamics is concerned, that all the reactions involved in the mechanism are possible in the temperature range considered. In addition, an increase of the temperature leads to a decrease of the

equilibrium constant, agreeing, therefore, with the thermodynamic laws since all the considered reactions are exothermic. The results, as presented here, give the final equilibrium state of the considered system but no information about the reaction mechanism.

TABLE 1

Comparison between the predicted and the literature values of the Gibbs energy as a function of the temperature for MgOHCl

T (K)	$\Delta H_{f.\text{literature}}$ (kcal/mol)	$\Delta G_{f.\text{literature}}$ (kcal/mol)	$\Delta G_{f.\text{predicted}}$ (kcal/mol)
298.15	–191.199	–174.773	–174.68
400	–191.080	–169.313	–168.840
500	–190.868	–163.893	–163.271
600	–190.555	–158.526	–157.563
700	–190.140	–153.219	–152.804
800	–189.623	–147.979	–147.933
900	–189.006	–142.809	–143.114
1000	–190.346	–137.544	–139.691

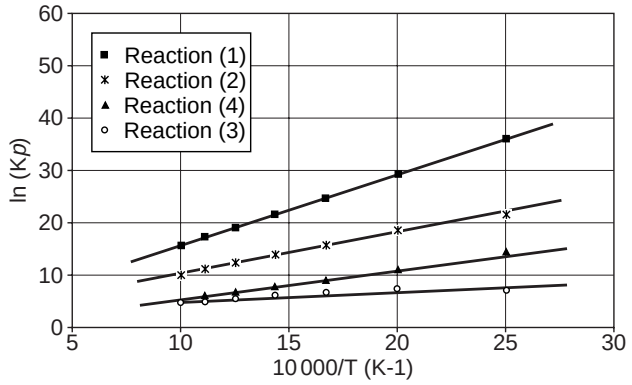


Figure 1

Equilibrium constant as a function of the temperature.

2 EXPERIMENTAL

This study deals with the formation of calcium hydroxichloride from a solid mixture of hydrated lime and calcium chloride. The experimental observations made on this reaction are very important, as far as the reaction mechanism of HCl capture and the analysis of the reaction products are concerned. An X-ray diffractometer, an electron microscope and a thermobalance were used to detect the formation of CaClOH, and are proposed for the elaboration of a method to analyze qualitatively and quantitatively calcium chloride, calcium hydroxide and calcium hydroxichloride.

The possibility that $Ca(OH)_2$ and $CaCl_2.2\,H_2O$ form a solid mixture was investigated by physically mixing these products, by simple contact at room temperature. Three mixtures having the following mass compositions have been prepared:

20% $Ca(OH)_2$ - 80% $CaCl_2.2\,H_2O$

50% $Ca(OH)_2$ - 50% $CaCl_2.2\,H_2O$

80% $Ca(OH)_2$ - 20% $CaCl_2.2\,H_2O$

It is important to prepare these solid mixtures just before the analysis. Bi-hydrated calcium chloride, $CaCl_2.2\,H_2O$, of analytical grade from *Prolabo* (France) and $Ca(OH)_2$ supplied by *Lhoist* (Belgium) were used.

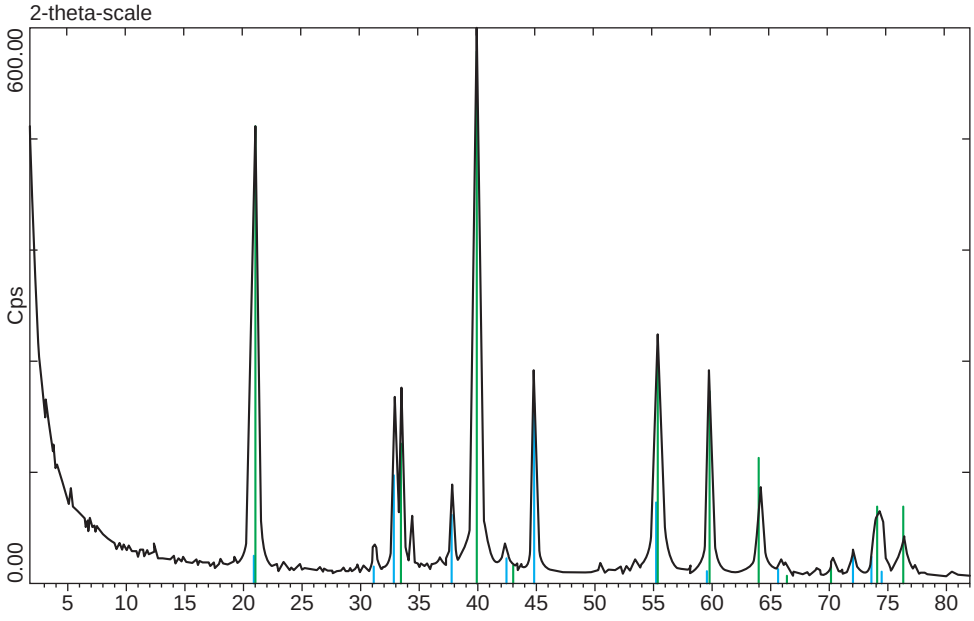
3 DISCUSSION

As mentioned above, three different techniques were used to study the evolution of the solid mixtures and to identify the reaction products, namely X-ray diffraction, electron microscopy and thermogravimetry.

3.1 X-ray diffraction

The X-ray diagrams of the above mentioned mixtures are shown in Figures 2 to 4 and the main observations are summarized in Table 2. For all cases considered, this table shows that after 30 minutes, a new solid phase is detected, which is identified as being calcium hydroxichloride. This compound appears to be the major phase incorporated in the solid solution after 24 hours, whereas $CaCl_2.2\,H_2O$ disappears completely. The case corresponding to 20% $Ca(OH)_2$-80% $CaCl_2.2\,H_2O$ (Fig. 4) seems to be particularly interesting since, despite the excess $CaCl_2.2\,H_2O$, the latter disappears entirely from the X-ray spectrum, which corresponds, in fact, to that of pure CaClOH. The mass balance is consequently not respected. No satisfactory formulation could be given to explain this evolution, except to assume that calcium chloride undergoes a transition toward an amorphous structure which might not be detected by X-ray diffraction.

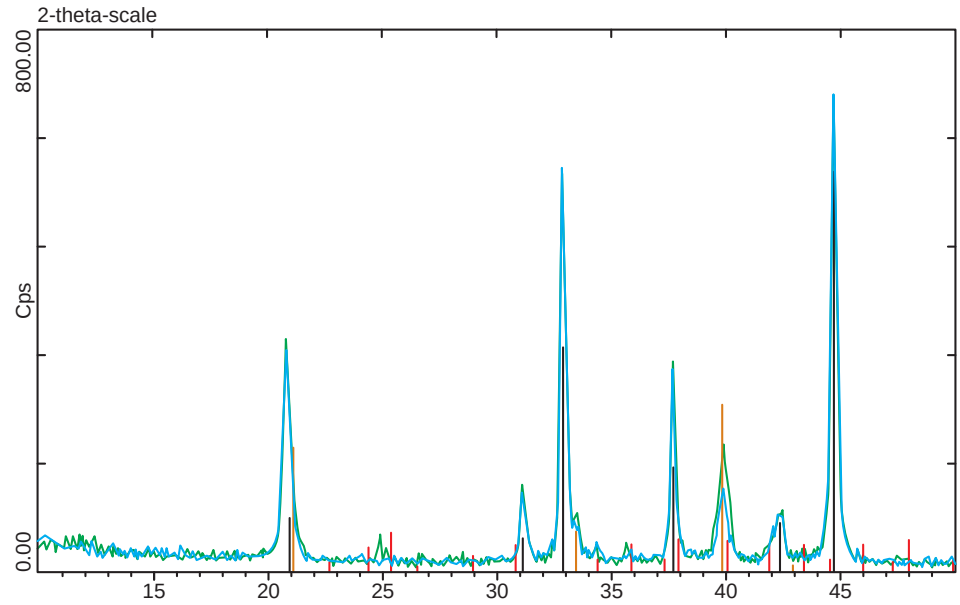
The spectrum represented in Figure 3 and corresponding to the case 50% $Ca(OH)_2$-50% $CaCl_2.2\,H_2O$, shows a number of spectral lines which could not be accurately attributed to known compounds.



$Ca(OH)_2$ 80/20
4-0733I $Ca(OH)_2$ Portlandite, syn (WL: 1.7890Ao)
36-0983 I CaClOH Calcium Chloride Hydroxide (WL: 1.7890Ao)

Figure 2

X-ray diffraction spectrum of a 80% $Ca(OH)_2$-20% $CaCl_2$ sample.



36-0983 I CaClOH Calcium Chloride Hydroxide (WL: 1.7890Ao)
$Ca(OH)_2/CaCL_2$ $T = 0.5^H$
$Ca(OH)_2/CaCL_2$ $T = 33^H$
2-0280I $Ca_4Cl_2O_3$ $15H_20$ Calcium Oxide Chloride Hydrate (WL: 1.7890Ao)
4-0733I $Ca(OH)_2$ Portlandite,syn (WL: 1.7890Ao)

Figure 3

X-ray diffraction spectrum of a 50% $Ca(OH)_2$-50% $CaCl_2$ sample.

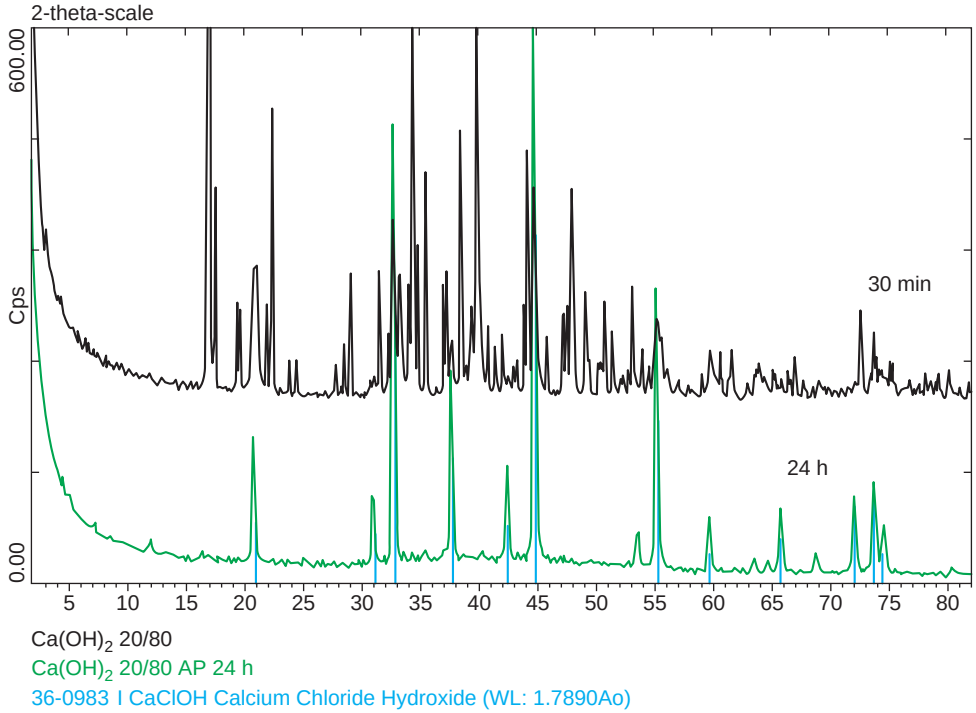


Figure 4

X-ray diffraction spectrum of a 20% $Ca(OH)_2$-80% $CaCl_2$ sample.

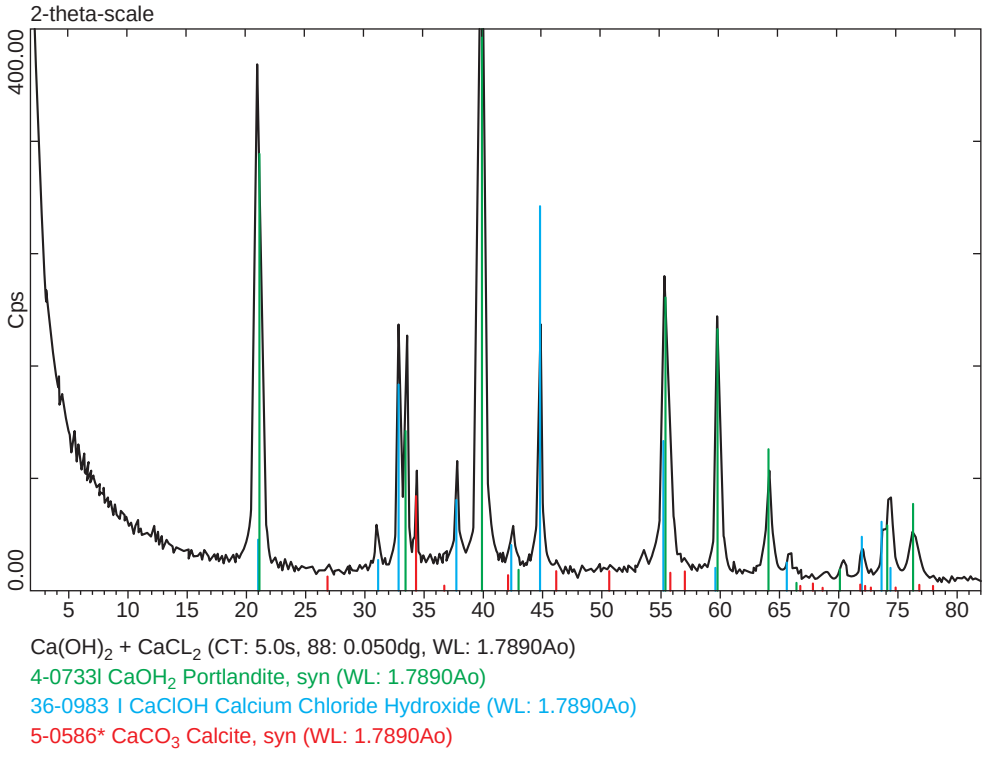


Figure 5

X-ray diffraction spectrum of a $Ca(OH)_2$ sample exposed to a HCl gas stream.

Two assumptions might however be formulated. The presence in the mixture of either an hydroxichloride phase with chemical formula $Ca_4Cl_2(OH)_6$, or a chlorite phase with the formula $Ca(ClO)_2.H_2O$. These spectral lines, which disappear after 15 hours, might correspond to an intermediate product formed during the formation of CaClOH.

TABLE 2

Summary of the results given by X-ray diffraction spectra

$Ca(OH)_2$-$CaCl_2$ (%)		30 min	24 h
20-80	$CaCl_2$-2 H_2O $Ca(OH)_2$ CaClOH	predominant phase few few	none none only phase present
50-50	$CaCl_2$-2 H_2O $Ca(OH)_2$ CaClOH	none present predominant phase	none present predominant phase
80-20	$CaCl_2$-2 H_2O $Ca(OH)_2$ CaClOH	none predominant phase present	none predominant phase present

Following the XRD analysis of the reagent grade mixtures, a sample of $Ca(OH)_2$ exposed to a flow of HCl stream in a drop tube furnace was prepared for XRD analysis. The operating conditions were 1000 ppm HCl, 250°C reaction temperature and 500 ms residence time in the reactor. It appears from the XRD spectrum presented in Figure 5, that no calcium chloride is formed, since the only detected phase containing chlorine is calcium hydroxichloride. Hence, with excess $Ca(OH)_2$, hydrated lime and hydrochloric acid undergo the following reactions:

$$Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O \quad (6)$$

$$Ca(OH)_2 + HCl \rightarrow CaClOH + H_2O \quad (7)$$

$$Ca(OH)_2 + CaCl_2 \rightarrow 2\ CaClOH \quad (8)$$

These results seem to suggest that calcium hydroxichloride is the only reaction product formed during the dechlorination process, as long as the calcium hydroxide is not completely consumed.

3.2 Electron Microscopy

An electron microscope has been used to obtain visual information on the transformations detected earlier by X-ray diffraction. Figures 6 and 7 are references and represent calcium chloride and calcium hydroxide taken separately. The same solid mixtures corresponding to 20% $Ca(OH)_2$-80% $CaCl_2.2\ H_2O$ have been used and observed over a period of three days. It can be seen that the aspect of the samples has changed during the experiment as shown by Figures 8, 9 and 10. The first picture (Fig. 8) corresponds to the first day and shows a situation that is somewhat difficult to interpret. Hence, a question might be asked. Could this be considered as a partial deliquescence or the appearance of a new phase? This situation nevertheless disappears on the third day (Fig. 10) as a population of small crystals, which were not present in the reference picture, can be observed.

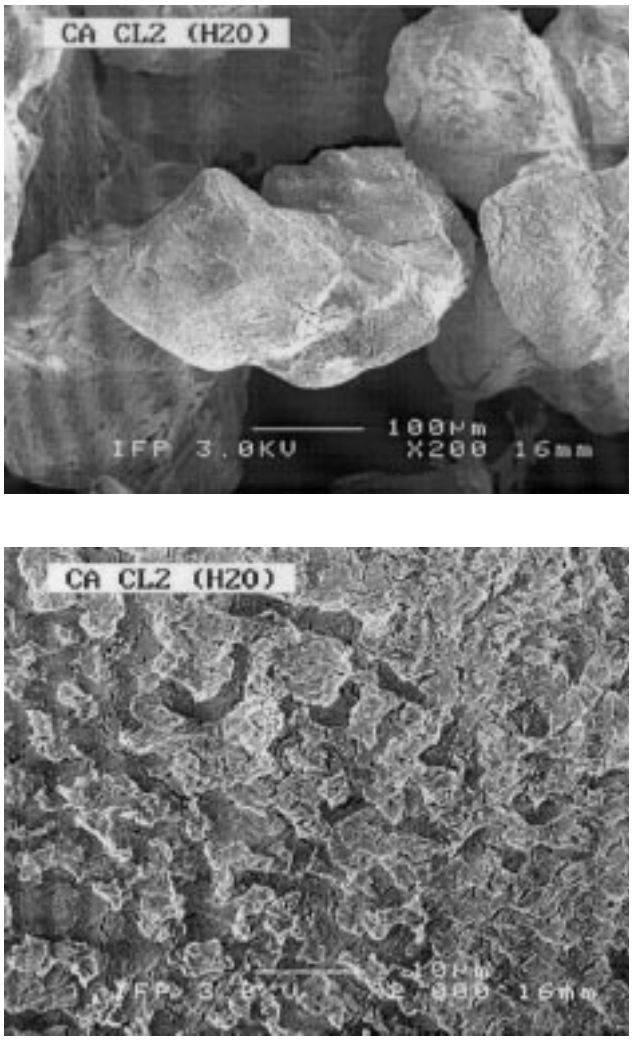


Figure 6

$CaCl_2$-2 H_2O as seen with an electron microscope.

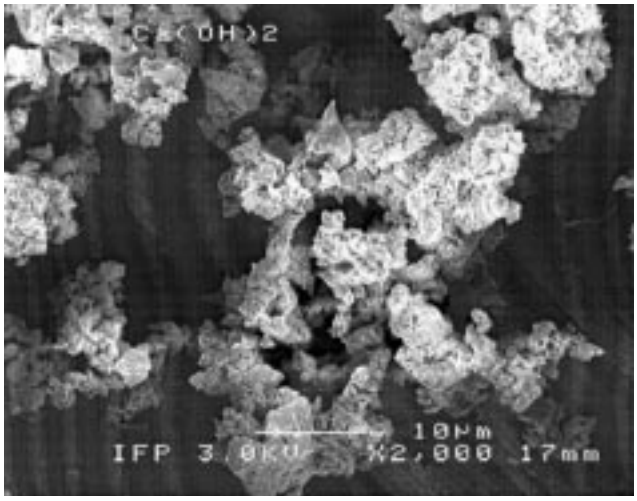


Figure 7

$Ca(OH)_2$ as seen with an electron microscope.

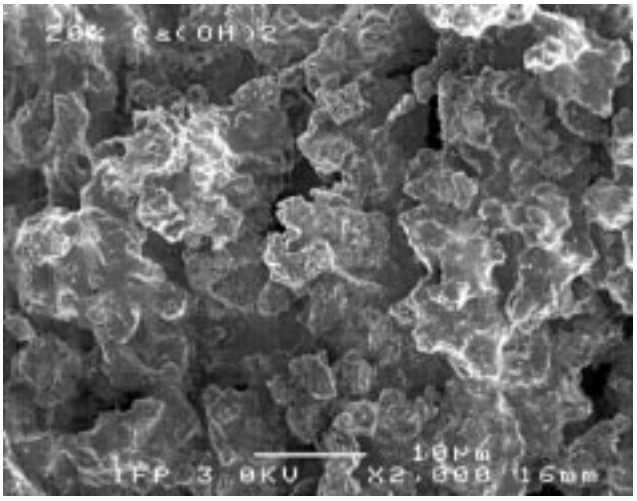


Figure 8

20% $Ca(OH)_2$-80% $CaCl_2$-2 H_2O as seen with an electron microscope. 1st day.

3.3 Thermogravimetry

The elementary analysis of chlorine is not sufficient to evaluate the extent of reaction conversion because several compounds having different molar ratio Ca/Cl might be present in the reaction products. The thermogravimetric analysis (TGA) under nitrogen stream coupled to the digital scan calorimetry (DSC) can provide information complementary to XRD as suggested by Jozewicz *et al.* [8]. They observed endothermic peaks between 530°C and 590°C, probably related to the decomposition of calcium hydroxichloride obtained when exposing $Ca(OH)_2$ to HCl.

A few milligrams (between 10 and 20 mg) of a solid mixture containing 80% $Ca(OH)_2$ and 20% $CaCl_2.2\,H_2O$ were prepared and analyzed the same day by thermogravimetry. The resulting thermogram has shown a series a weight losses, as illustrated by Figure 11. The mass balance suggests the following reaction mechanism:

$$2\,CaClOH.2\,H_2O \rightarrow 2\,CaClOH + 2\,H_2O \quad (9)$$

$$Ca(OH)_2 \rightarrow CaO + H_2O \quad (10)$$

$$2\,CaClOH \rightarrow CaO.CaCl_2 + H_2O \quad (11)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (12)$$

where the first loss corresponds to the dehydration of hydrated calciumhydroxichloride formed through

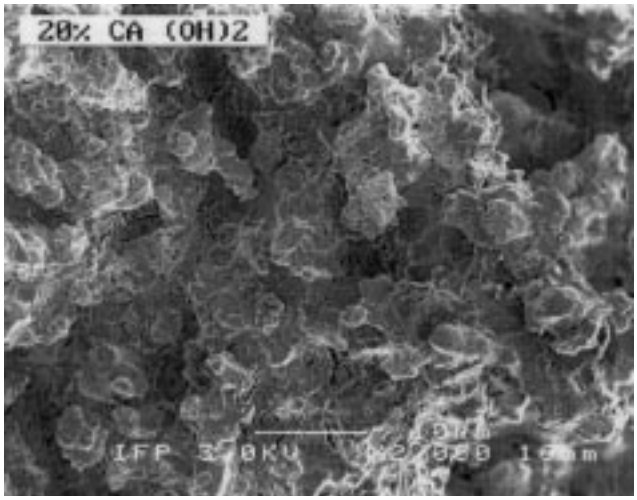


Figure 9

20% $Ca(OH)_2$-80% $CaCl_2$-2 H_2O as seen with an electron microscope. 2nd day.

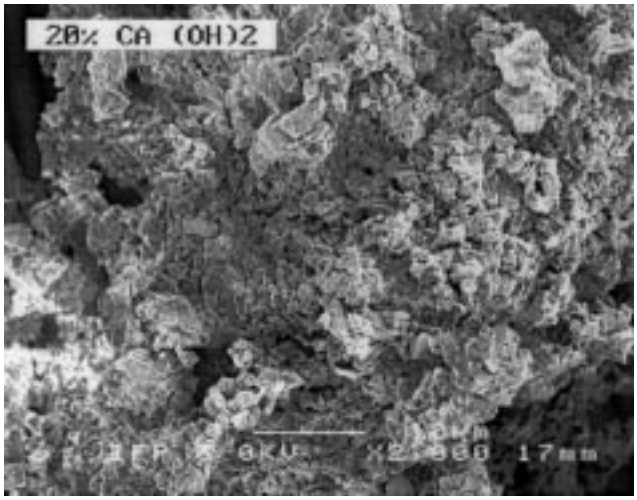
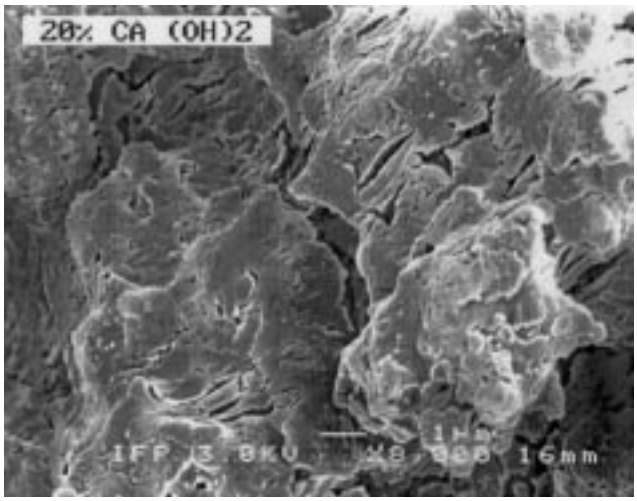
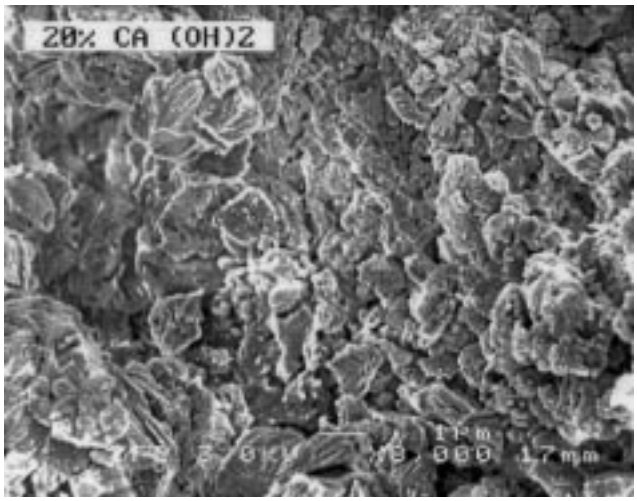


Figure 10

20% $Ca(OH)_2$-80% $CaCl_2$-2H_2O as seen with an electron microscope. 3rd day.





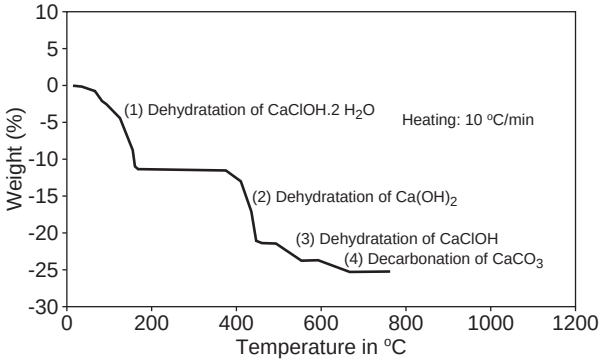


Figure 11

TGA scan thermogram of a sample containing 80% $Ca(OH)_2$-20% $CaCl_2$-2 H_2O.

Reaction (3), the second loss to the dehydration of the remaining calcium oxide, the third to the decomposition of calcium hydroxichloride formed through Reaction (9) and the last to the decarbonatation of calcium carbonate initially present in the mixture. This reaction mechanism is confirmed by an infrared analysis coupled to the thermobalance. Figures 12 and 13 representing the wave length as a function of time indeed show the presence of H_2O and CO_2 in the flue gas at the exit of the thermobalance. It can be shown that the values of weight losses determined experimentally agree fairly well with those evaluated theoretically through Reactions (9), (10), (11) and (12).

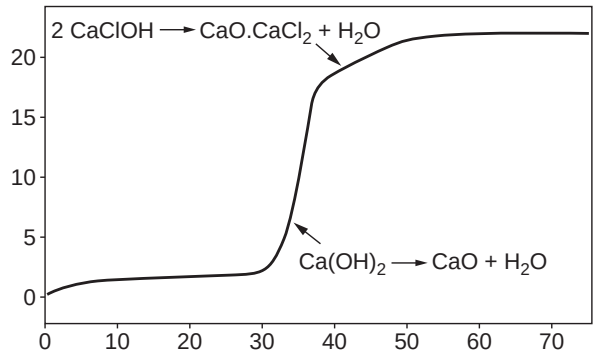


Figure 12

Wave length as a function of time for the detection of H_2O.

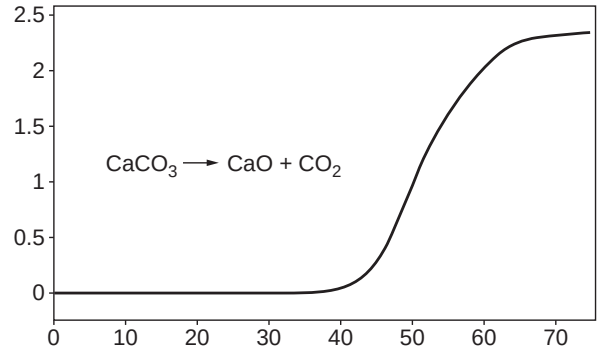


Figure 13

Wave length as a function of time for the detection of CO_2.

A differential scan calorimeter (DSC) was used simultaneously with the TGA, and the results are shown in Figure 14. It can be seen that to each of the above mentioned reactions, corresponds an endothermic peak, the area of which is closely related to the reaction enthalpy. It is therefore possible to confirm Reaction (11) by evaluating the enthalpy of formation of $CaO.CaCl_2$ and matching it with values reported in the literature. A graphical integration of the peak corresponding to Reaction (11) between 479°C and 564°C gives a value of ΔH_R equal to 23.72 kcal/mol. Since:

$$\Delta H_R = \sum(\Delta H_f)\text{prod} - \sum(\Delta H_f)\text{react} \qquad (13)$$

one can deduce the enthalpy of formation of $CaO.CaCl_2$ from the following equation:

$$\Delta H_{f,\text{CaO.CaCl}_2} = 2.\Delta H_{f,\text{CaClOH}} + \Delta H_R - \Delta H_{f,\text{H}_2\text{O}} \qquad (14)$$

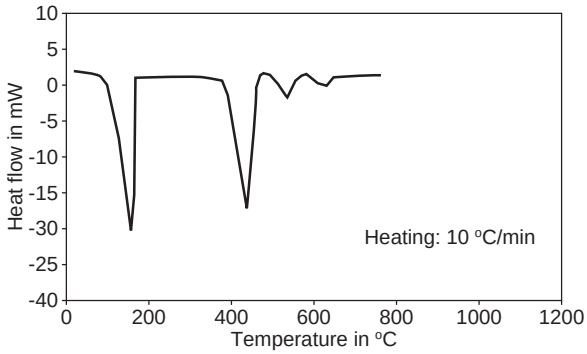


Figure 14

Differential scan calorimetry of a sample containing 80% $Ca(OH)_2$-20% $CaCl_2$-2 H_2O.

A value of –352.6 kcal/mol has been found. This result agrees fairly well with the value of –347.3 kcal/mol predicted by Mostafa's model (11).

CONCLUSION

The analytical study conducted by means of X-ray diffraction, electron microscopy and thermogravimetry has shown that the reaction of calcium hydroxide with hydrochloric acid leads to the formation of calcium hydroxichloride. It appears that calcium chloride is unstable in the presence of calcium hydroxide and that its formation is subsequent to the total conversion of $Ca(OH)_2$ into CaClOH. This study has also shown the possibility of using a thermobalance to evaluate the amount of CaClOH formed.

ACKNOWLEDGMENT

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