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Hydrogen Chloride (HCl) Absorption by Raw Meal and Raw Meal Compounds, using In-situ HCl Generation and TGA-FTIR Tests

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Graphical abstract
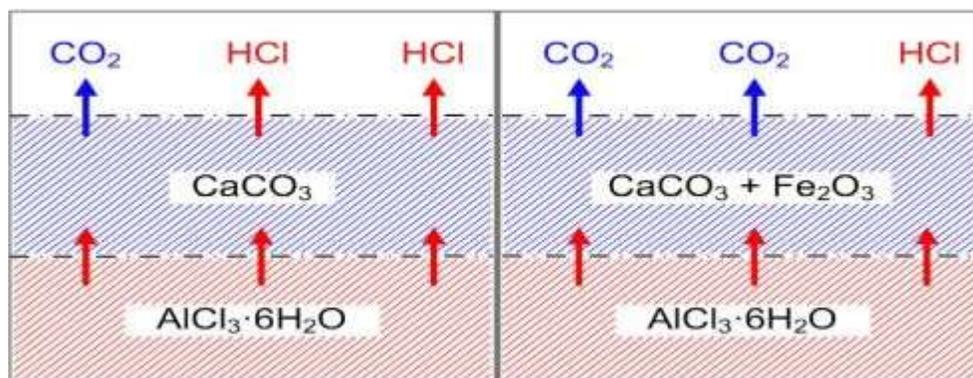
Highlights

- HCl absorption by cement raw meal and raw meal constituents below 400℃.
- HCl absorption potential of raw meal is significantly higher than that of reagent grade $CaCO_3$.
- Fe_2O_3 promotes the chlorination of reagent grade $CaCO_3$
- SiO_2 and Al_2O_3 do not promote the chlorination of reagent grade $CaCO_3$

ABSTRACT HCl emission control optimization from cement plants requires a quantification of the HCl absorption capacity of raw meals (mixtures of fine particles of raw materials) and the determination of raw meal constituent effects on HCl capture below 400℃. This work reports lab data obtained by ramping temperature tests using a standard TGA-FTIR set-up, a thermally degradable solid HCl source ($AlCl_3 \cdot 6H_2O$), industrial raw meals, and mixtures of reagent grade raw meal constituents (SiO_2, $CaCO_3$, Fe_2O_3, and Al_2O_3). The lab data showed that industrial raw meals had significantly higher HCl absorption capacity than reagent grade $CaCO_3$. The presence of Fe_2O_3 promoted HCl capture by $CaCO_3$ between 90℃ and 350℃. The HCl absorption by raw meals was higher when the HCl source was dispersed rather than when it was placed below the raw meals.

KEYWORDS: HCl; Absorption; Cement; $CaCO_3$; Fe_2O_3; Low temperatures

1. **Introduction**

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HCl is a gaseous industrial pollutant with serious environmental impact due to its high toxicity. In humans, HCl inhalation can result in respiratory system irritation, and death in the case of high HCl concentrations [1, 2]. Furthermore, it is related to the formation of photochemical smog, acid rain, decay of structures, e.g., limestone buildings, and dissolution of minerals, e.g., limestone [3]. Based on the affected geographical area, HCl can be considered both a local and regional pollutant due to its high solubility in water that allows for its washing out by rain and moisture in the air [1, 4].

A number of cement plants currently need emission abatement to comply with applicable HCl emission limits. On-site measurements at cement plants with high HCl concentrations in the preheater effluent gas showed the presence of net HCl release and net absorption zones in the cement manufacturing process. The net HCl release zones comprise the rotary kiln and upper cyclones (260-600℃) of preheater towers.

The mechanism of HCl release in the upper cyclones of the preheater tower is not completely understood. The identification of HCl release mechanisms in preheater towers is difficult due to the low chlorine content of raw meal and use of naturally occurring materials with varying composition. A number of potential HCl release mechanisms can be suggested. These comprise the thermal dissociation of salts and salt hydrates that are present as impurities in raw materials, e.g. $MgCl_2 \cdot 6H_2O$, or are formed during the cement manufacturing process (NH_4Cl), organic matter reaction with inorganic chlorides, e.g., carboxylic acids reaction with KCl or NaCl, and gas – solid reactions of inorganic chlorides (KCl, $CaCl_2$ and NaCl) with flue gas compounds [5].

On the other hand, the literature data support that HCl formation in combustion zones (calciner and kiln) can be related to reaction of alkali chlorides with flue gas compounds [6] and to the thermal decomposition of organic chlorides, e.g. polyvinyl chloride (PVC) [7]. Industrial results indicated a close correlation between SO_2 and HCl concentrations in kiln bypass gas which makes important the following reaction for the HCl formation in kiln:

$$2KCl + SO_2 + H_2O \rightarrow 2HCl + K_2SO_3 \qquad (1)$$

The conventional HCl emission control methods comprise the empirical utilization of scrubbing phenomena in the grinding unit of raw materials, $Ca(OH)_2$ injection into flue gas, and acidic gases scrubber installation. The most important HCl absorption zone to understand from an emissions control perspective is the post-preheater tower units (gas condition tower, particle filters, and grinding installations) covering the temperature range 90-400℃. On-site data showed that the HCl reduction in particle filters with an inlet gas HCl concentration of ~ 34 mg/Nm^3 increased from 50% to 63% with a decrease of operating temperature from 210℃ to 150℃. Furthermore, the HCl scrubbing efficiency of an operating raw mill with flue gas passing through was observed to be close to 100% with a flue gas inlet HCl concentration of 25mg/Nm^3. The on-site data thus indicated that preheater dust and raw meal act as HCl sorbents. Interestingly, the scrubbing in particle filters and raw mill corresponded to active compound (assumed to be $CaCO_3$) conversions as small as 0.04% and 0.005 %,

respectively. These observations indicate a need for a more systematic investigation of HCl absorption on raw meals and raw meal constituents.

2. Material and Methods

The HCl absorption on raw meals and on constituents of raw meals was investigated in a TGA-FTIR instrument [5] using in-situ HCl generation by the thermal decomposition of $AlCl_3 \cdot 6H_2O$ [8]

$$AlCl_3 \cdot 6H_2O(s) \rightarrow \frac{1}{2}Al_2O_3(s) + 3HCl(g) + 4.5H_2O(g) \quad (2)$$
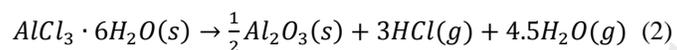
in the temperature range 90-350°C [8, 9]. The HCl source and the absorbing compounds (raw meal or raw meal constituents) were used either mixed or placed in the instrument as a layered structure where the absorbing compounds lay above the HCl source. A ramping temperature with heating rate 15°C/min was used to cause HCl release. The carrier gas flow rate was 50 Nml/min. The HCl absorption was studied both directly through the HCl signal and indirectly through the CO_2 signal caused by reaction between HCl and carbonaceous compounds in the raw meal and its constituents. The composition and physical properties of the used materials and mixtures were presented by Pachitsas (2018) [5].

3. Results and Discussion

The evaluation of the HCl absorption capacity of two industrial raw meals (RM-A and RM-B) was based on tests using a mass ratio of raw meal to $AlCl_3 \cdot 6H_2O$ of 9.2. Figure 1 shows the HCl release profile of a 62 mg $AlCl_3 \cdot 6H_2O$ sample with and without 570 mg of RM-A (layered structure).

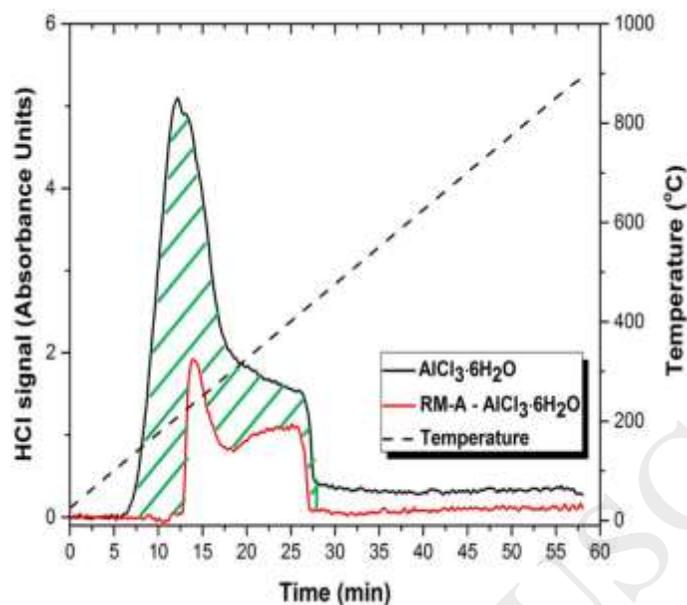Figure 1. HCl signals from pure $AlCl_3 \cdot 6H_2O$: 62mg, and RM-A - $AlCl_3 \cdot 6H_2O$ (layered sample structure): RM-A: 570mg and $AlCl_3 \cdot 6H_2O$: 62mg.

The experimental results (Figure 1 and Figure 2) showed that the raw meals absorbed significant amounts of HCl. CO_2 release was detected to occur simultaneously with HCl capture by raw meals. XRD analysis of raw meal samples exposed to HCl verified the formation of $CaCl_2$ as a product of HCl reaction with raw meal. Hence $CaCO_3$ may be presumed to be the active component in the raw meals, and the absorbed amounts of HCl correspond to conversions between 5.6% and 7.3%. These values are significantly higher than the active compound conversion from on-site tests ($< 0.04\%$, see above) or observed in fixed-bed tests ($\sim 0.15\%$) with raw meals at low temperatures (100-180℃) [10]. The absorption conditions in TGA-FTIR tests differ from those in fixed-bed tests absorbing HCl in the inlet gas. The reaction times for HCl absorption are very different: of the order of seconds for on-site and fixed-bed tests, and of the order of quarter hours for TGA-FTIR tests. The melting $AlCl_3 \cdot 6H_2O$ may have significant influence. Also much higher local HCl and H_2O concentrations released from decomposition of $AlCl_3 \cdot 6H_2O$ are expected to be important.

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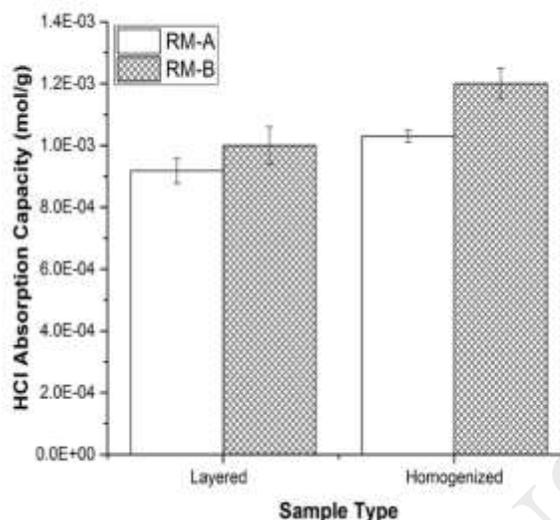
Figure 2. Specific HCl absorption capacities of RM-A and RM-B, using mass ratio of raw meal to $AlCl_3 \cdot 6H_2O$: 9.2.

Figure 2 shows that dispersion of the HCl source in the sample increases the maximum HCl absorption capacities of raw meals. This may be related to the low melting point of $AlCl_3 \cdot 6H_2O$ (100℃ [11]) and its thermal dissociation temperature window (90-350℃ [8, 9]). The liquefied HCl source initially wets the raw meal particles and in a second stage the main thermal dissociation (HCl release) occurs. Therefore, the dispersed HCl source gives a larger contact interface to the reactants, and consequently it increases the conversion of raw meal.

The results show that RM-B has 9% and 17% higher HCl absorption capacities than RM-A in the case of 'layered' and 'homogenized' samples, respectively. The main differences of the raw meals in composition and physical properties are related to BET area, and contents of Fe_2O_3 and MgO. BET area, Fe_2O_3, and MgO ratios of RM-B to RM-A are 1.26, 0.76 and 1.9, respectively. The tested raw meals had identical $CaCO_3$ content.

The effects of these parameters on HCl absorption cannot be evaluated quantitatively based on the available data. However, both TGA-FTIR and fixed-bed [10] tests showed that the raw meal with the larger BET area also had larger HCl absorption capacity.

The evaluation of the effect on HCl absorption by raw meal constituents was based on tests using pure reagent grade compounds separately or mixed. These tests used a mass ratio of sample to $AlCl_3 \cdot 6H_2O$ of 14.2 in a layered structure.

The obtained lab data (see Figure 3 and Table 1) show that RM-B has significantly higher HCl absorption capacity than reagent grade $CaCO_3$, and the presence of Fe_2O_3 promotes $CaCO_3$ chlorination in the case of reagent grade

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mixtures. However, a direct correlation of Fe_2O_3 content with HCl absorption capacity is not apparent at the used conditions. In addition, SiO_2 acts as an inert compound in the temperature range 90-350℃, Al_2O_3 does not promote HCl absorption, and pure Fe_2O_3 reacts with HCl but to a much lesser extent than pure $CaCO_3$.
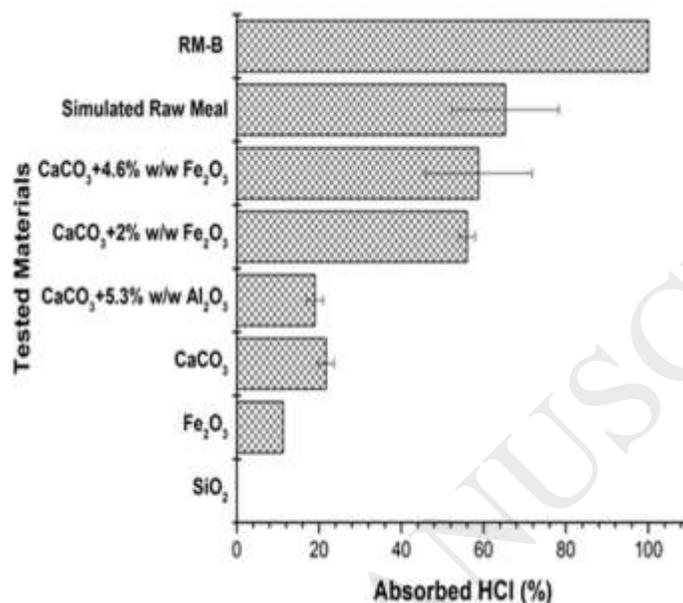
Figure 3. Percent of the released HCl from $AlCl_3 \cdot 6H_2O$ that is absorbed by the tested materials, using mass ratio of tested material to $AlCl_3 \cdot 6H_2O$: 14.2.

Table 1. Relative HCl absorption capacity and BET area normalized by values for reagent grade $CaCO_3$. The relative values are unitless. The absorption capacities before normalization are in mol/g $CaCO_3$ in the sample and BET areas before normalization are in m^2/g of the sample.

Tested materials	Relative HCl capacity ratio	Relative BET area ratio
$\dfrac{RM-B}{CaCO_3}$	5.63	22
$\dfrac{Simulated\ Raw\ Meal}{CaCO_3}$	3.68	2.2
$\dfrac{CaCO_3 + 4.6\%\ w/w Fe_2O_3}{CaCO_3}$	2.85	2.22
$\dfrac{CaCO_3 + 2\%\ w/w Fe_2O_3}{CaCO_3}$	2.64	1.43
$\dfrac{CaCO_3 + 5.3\%\ w/w Al_2O_3}{CaCO_3}$	0.92	1.77

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The formation of iron chloride species (gaseous and solid) as products of HCl - Fe_2O_3 reaction in the temperature range 140-400°C is reported [12, 13]. Table 2 shows some indicative reactions which are mentioned in literature or are thermodynamically possible based on Gibbs free energy minimization at equilibrium state (software FactSage 7). In our tests the concurrent release of water could lead to formation of more or less liquefied species, at least at the lower temperatures. The formation of iron chlorides which react via ion exchange with CaO and $CaCO_3$ is also reported in the temperature range 200-500°C [14, 15] in applications of CaO - Fe_2O_3 and $CaCO_3$ - Fe_2O_3 catalysts for dechlorination of organic chlorides.

Table 2. Iron chlorides formation by Fe_2O_3 – HCl reactions in the temperature range 100-350°C.

Reaction	Source
$\frac{1}{2}Fe_2O_3(s) + 3HCl(g) \rightarrow FeCl_3(s) + \frac{3}{2}H_2O(g)$ T < 235°C	FactSage 7
$\frac{1}{2}Fe_2O_3(s) + 3HCl(g) \rightarrow FeCl_3(g) + \frac{3}{2}H_2O(g)$ T > 316°C	FactSage 7
$Fe_2O_3(s) + 6HCl(g) \rightarrow Fe_2Cl_6(g) + 3H_2O(g)$	Gregory [12]
$Fe_2O_3(s) + 2HCl(g) \rightarrow 2FeOCl(s) + H_2O(g)$	Gregory [12]
$6FeOCl(s) \rightarrow 2Fe_2O_3(s) + Fe_2Cl_6(g)$	Gregory [12]
$Fe_2O_3(s) + 6HCl(g) \rightarrow 2H_2OFeCl_3(g) + H_2O(g)$	Gregory [12]
$Fe_2Cl_6(g) \rightarrow 2FeCl_3(g)$ T > 300°C	Rustad and Gregory [13]
$Fe_2Cl_6(g) \rightarrow 2FeCl_2(s) + Cl_2(g)$	Rustad and Gregory [13]

Table 3 shows a group of reactions which can explain the enhancement of HCl absorption in presence of Fe_2O_3 through the formation of iron chlorides. Furthermore, in the case of RM-B tests the molar ratio of the absorbed HCl to the released CO_2 is 4 which differs from the stoichiometry of the following direct reaction of HCl with $CaCO_3$:
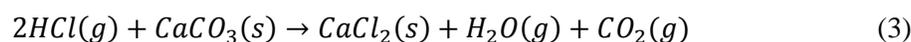
$$2HCl(g) + CaCO_3(s) \rightarrow CaCl_2(s) + H_2O(g) + CO_2(g) \qquad (3)$$

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Table 3. Potential reactions that can explain the HCl absorption between 100℃ and 350℃, involvement of iron chlorides, and formation of $CaCl_2$.

Reaction	Source
$2FeCl_3(g) + 3CaCO_3(s) \rightarrow 3CaCl_2(s) + Fe_2O_3(s) + 3CO_2(g)$	FactSage 7
$FeCl_2(s) + CaCO_3(s) \rightarrow CaCl_2(s) + FeCO_3(s)$	FactSage 7
$FeCO_3(s) + 2HCl(g) \rightarrow FeCl_2(s) + H_2O(g) + CO_2(g)$	FactSage 7

Thus, the Fe_2O_3 effect on HCl absorption by $CaCO_3$ may be caused by the formation of iron chlorides as intermediate species in the temperature range 90-350℃ which react with $CaCO_3$ and release CO_2 in a second step.

It may be mentioned that secondary CO_2 releases from RM-B / $AlCl_3$·6 H_2O tests were detected at temperatures above 350℃ where no more HCl was released from the aluminum chloride. This indicates that some of the products of primary HCl absorption react further with the tested materials at higher temperatures.

The different mixtures of reagent grade compounds have BET areas that are generally of the order of twice the BET area of pure $CaCO_3$ (Table 1) even though pure $CaCO_3$ is the dominant constituent of the mixtures. This may be caused by either a grinding and diminution effect on $CaCO_3$ particles during mixing or by the minor compound having very smaller particle sizes than the $CaCO_3$. The larger BET areas of the mixtures relative to pure $CaCO_3$ do not seem to be directly correlated with the increased ratios between absorbed amounts of HCl on mixtures and pure $CaCO_3$. Hence, we conclude that it is the mixed-in compounds which cause changes in absorption of HCl on $CaCO_3$, not concurrent change in BET area.

The one exception may be for raw meal RM-B. The BET area is so much larger, signifying much smaller particles, that some of the increase in absorbed HCl compared to simulated raw meal may simply be due to better accessibility of solid, active compounds.

4. Conclusions

The main conclusions of this work can be summarized as follows:

- Industrial raw meals can absorb significant amounts of HCl in the temperature range 90-350℃. The formation of $CaCl_2$ and CO_2 release were verified.

- Industrial raw meals have significantly higher HCl absorption potential than the reagent grade $CaCO_3$ and mixtures of reagent grade compounds.

- Fe_2O_3 promotes HCl absorption by reagent grade $CaCO_3$ between 90℃ and 350℃.

- SiO_2 and Al_2O_3 do not promote the HCl absorption by reagent grade $CaCO_3$ between 90℃ and 350℃.

- The BET areas of artificial absorbent mixtures relative to pure $CaCO_3$ have at most a secondary influence on enhancement of HCl absorption.

- The dispersion of HCl source in the raw meals gives higher HCl absorption potentials than those of the layered samples.

- The active compound ($CaCO_3$) conversions in TGA-FTIR tests were between 5.6% and 7.3%, much higher than in short time on-site and fixed-bed reactions. This implies that the HCl absorption conditions differ from that in on-site tests. Therefore, TGA-FTIR tests may not be appropriate for assessing the maximum HCl absorption potential of raw meals at industrial conditions.

Acknowledgement

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