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**RESEARCH ARTICLE**

# Improvement of Lime Reactivity towards Desulfurization by Hydration Agents

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**Abstract:** Three hydration agents namely calcium acetate, ammonium acetate and citric acid were used to augment lime's reactivity through hydration. The performance of these agents was compared with pure distilled water. The produced sorbents were tested in a pH-stat facility and a fixed bed apparatus which simulate wet and dry flue gas desulfurization respectively. It was observed that all agents improved lime's reactivity by a higher percentage than water and that calcium acetate was the best agent, followed by ammonium acetate. Dissolution and hydrolysis of the calcium and acetate ions were thought to be the cause of these results while for acidic agents, high concentration of the hydrogen ion was the cause of the improved performance. BET surface area analysis, XRD and SEM imaging were used to explain the results.

**Keywords:** Hydration agents, Reactivity, Sorption capacity, Surface area

## Introduction

Energy conversion today is based largely on the burning of fossil fuels, of which coal and oil contain a large amount of sulfur (S). During combustion, the S is released to the atmosphere as sulfur dioxide ($SO_2$). To a large extent, the $SO_2$ is subsequently converted into sulfuric acid ($H_2SO_4$), resulting into acid rain. Over the years, the allowed $SO_2$ emission level has been lowered, thereby necessitating an increased efficiency of desulphurization plants. A lot of studies have been conducted to reduce the amount of $SO_2$ in air.

The most commonly used material for flue gas desulfurization (FGD) is limestone due to its availability and price. Limestone is mainly made up of calcite ($CaCO_3$) which, although is alkaline in nature, is not reactive enough to remove a desirable amount of sulfur dioxide from flue gases. Therefore, limestone is usually calcined to quicklime (CaO) depending on the carbon dioxide ($CO_2$) partial pressure. Quick lime reactivity is usually higher than that of limestone. Many researchers attributed this increase in reactivity to the increase in surface area and porosity of the calcinations product[1]. Also, quicklime's increase in reactivity can be associated with its superior chemical properties as compared to limestone. To further increase the reactivity, quicklime is usually hydrated to slaked lime ($Ca(OH)_2$) which has superior surface area and porosity compared to quicklime. The hydration process is mostly conducted by using deionised water as the hydration agent.

Some important parameters affecting the desulfurization process are: sorbent size, porosity and total surface area. Small pores are prone to plugging by sulfation products[2]. If lime (or limestone) absorbs $SO_2$, the internal structure of the lime is changed when these solid products are produced. Because the molecular volumes of $CaCO_3$, CaO, calcium sulfide (CaS) and calcium sulfate ($CaSO_4$) are 36.9, 16.9, 28.9 and 46.0 $cm^3/g$, respectively, the intra-particle pores become smaller in size and may be finally plugged by the product if the molecular volume of the product is larger than that of the reactant[3]. However, several studies have proved that the sorbents properties *e.g* surface area, improves greatly when the hydration agents contain salts *e.g* ammonium salts[4], copper acetate[5], sodium acetates[6], zinc acetate[7] and cobalt acetate[8]. Relatively new procedures using calcium acetate, water, copper catalysts supported on acid treated activated carbon, fly ash mixed with $Ca(OH)_2$ or CaO are gaining interest[9].

Both the addition of organic acids and the use of fine limestone can improve the $SO_2$ removal rate and the limestone utilization in FGD plants[10]. Carboxylic acid salts of calcium were previously identified to be excellent $SO_2$ and $NO_x$ concentration-reduction agents. The unique property of these compounds to calcine, forming highly porous, cenospheric CaO particles of superior physical structure (thin and porous walls, resembling ‘‘pop-corn’’- like structures) was observed[11]. The devolatilizing/decomposing organics have been shown to reduce $NO_x$ emissions, while the remaining solid $CaCO_3$/CaO structure reacts heterogeneously with $SO_2$. Furthermore, as most of these compounds are highly soluble in water they can either be dry or wet injected[2].

Calcium acetate and calcium magnesium acetate prove to be more efficient in desulfurization. They can be up to 4 times more efficient at desulfurization compared with similarly prepared limestone and dolomite sorbents[12]. Moreover, the hydrocarbon radicals generated during organic acetate decomposition permits the reduction of the $NO_X$ simultaneously to the $SO_2$ during coal combustion. This can have a significant impact on reducing the capital costs and the complexity of the effluent gas treatment. The high porosities exhibited by these particles greatly reduce the importance of the limiting resistance in gas–solid reactions and increase the sorbent utilization[11].

In this study, improvement of lime’s reactivity was investigated by the addition of three additives namely; ammonium acetate, calcium acetate and citric acid. The effects of these additives were compared to pure deionised water as the basic hydration liquid. Several methods have been developed for the evaluation of the suitability of sorbents for the sulphation process. They are based on the reaction of the sorbent with gaseous sulfur dioxide or an aqueous solution of sulfur dioxide ($H_2SO_3$ or $H_2SO_4$). When strong acids like sulfuric acid or hydrochloric acid are used, the reaction mechanism is close to that on a wet FGD plant equipped with air oxidation of the bisulphite ion[13]. Recently, ASTM developed a standard test method for the determination of total neutralizing capability of dissolved calcium and magnesium oxides in lime for FGD (ASTM C: 1318-95). This method recommends an acid titration procedure.

## Experimental

Natural limestone was mined in South Africa. The raw samples were crushed, ground and sieved to a particle size of utmost 200 μm. It was further calcined in an electric furnace at 900 °C for 4 hours. The other chemicals used were outsourced in local chemical stores. The experimental work is initiated by testing if the additives improved lime reactivity. This was done using a pH-stat method which simulates wet FGD and a fixed bed reactor which simulates dry FGD[14]. In a pH-stat method, 1.5 g of the sorbent (calcined lime), was dissolved into 200 mL of either distilled water or 0.1 M solution of the additives. The solution was put in a water bath set at 60 °C with a resolution of ±1 °C and agitated by a stirrer rotating at 225 rev/min. The pH in the beaker was measured by a pH electrode inserted in the solution and connected to a pH 200 controller supplied by Eutech Instruments with a resolution of ±0.01. A 1 M solution of HCl was titrated accordingly and the reactivity was determined from a recording of the volume of HCl added *versus* time. Each experiment was done at least twice and the average of the results taken. A plot of the amount of acid consumed *versus* time taken gives the reactivity of the sorbent depending on the rate-limiting step. Figure 1 below shows the pH-stat experimental apparatus used. Models used to describe the heterogeneous non-catalytic solid-fluid reaction mechanism falls into three main categories[15]:

- Grain models,
- Pore models
- Deactivation models

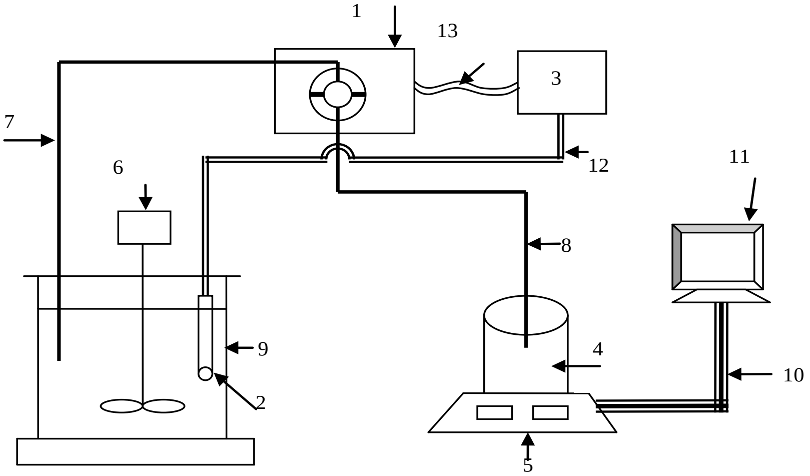


**Figure 1.** A schematic drawing of the experimental set-up. (1) Peristaltic pump, (2) pH electrode, (3) pH controller, (4) Acid solution Beaker, (5) Electronic balance, (6) Stirrer, (7,8) Plastic tubing, (9) Reaction vessel,(10) RS232 Cable, (11) Computer work station, (12) wiring for pH electrode, (13) Connection between pump and controller.

The grain model is relatively simple and largely used to describe heterogeneous non-catalytic solid-fluid reaction. This model assumes that the porous solid is made up of small non-porous grains, and each of these grains is converted according to the shrinking unreacted core model. In shrinking unreacted core model, spherical particles making up the grains are converted at a rate depending on the limiting step on which as derived and explained in[16];

- If the chemical reaction is the rate-limiting step

$$\frac{t}{\tau} = \left[1 - (1 - x)^{1/3}\right] \tag{1}$$

The reactivity will be given by a plot of [1-(1-x)^(1/3)] *versus* time .

- If the diffusion through the product layer is the rate-limiting step

$$\frac{t}{\tau} = \left[3 - 3(1 - x)^{2/3} - 2x\right] \tag{2}$$

The reactivity will be given by a plot of [3-3(1-x)^(2/3)-2x] *versus* time .

- If the mass transfer through fluid film is the rate limiting step

$$\frac{t}{\tau} = x \tag{3}$$

The reactivity will be given by a plot of x *versus* time. Where t is time taken (secs), x is the ratio of acid consumed at time t to total acid consumed (mL/mL) and τ is a constant depending on the reactants properties and the reaction process itself (secs).

Due to the nature of the experiments, the product layer will constantly be dislodged from the surface by the agitation therefore there will be minimum resistance due to diffusion through the product layer and thus it won't be the rate limiting step. Similarly, due to the fact that the fluid media is liquid in nature, mass transfer through fluid film will have a minimum effect on the overall reaction, therefore it will not be the rate limiting step. Furthermore, a lot of literature with similar experiments state that these types of reactions are chemically controlled[17]. Therefore, the reactivity constant was calculated by assuming that these reactions were chemically controlled.

To ascertain the increase in reactivity, a laboratory-scale fixed bed reactor (Figure 2) was used to simulate dry FGD. The reaction zone is contained in a 0.009 m inner diameter stainless steel tube fitted in a furnace for isothermal operation. 0.2 g of the sorbent material was packed in the center of the reactor supported by 0.03 g of glass wool. The reactor is heated up to desired temperature.

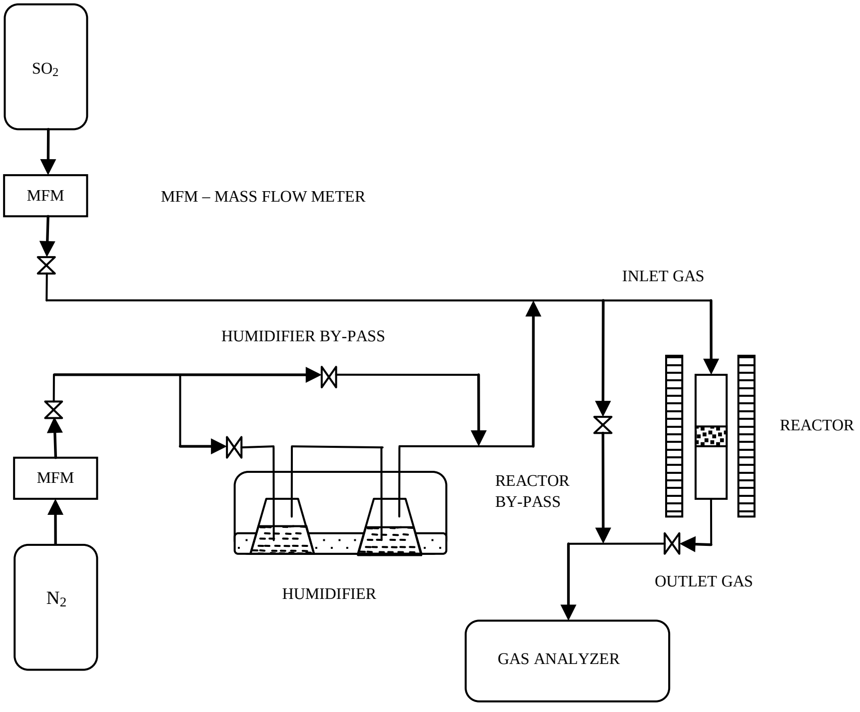


**Figure 2.** Schematic diagram of the experimental rig for laboratory fixed bed reactor

A nitrogen gas ($N_2$) stream was passed through a humidification system consisting of two 750 mL conical flasks immersed in a water bath at a set constant temperature for a specified humidity ratio depending on the partial pressure of the steam. This humidified stream was allowed through the reactor for 10 minutes to humidify the sorbent. Humidified sorbents are more effective for desulfurization because $SO_2$ is hydrated by the adsorbed water molecules on the sorbent surface before reacting[14]. After humidification, nitrogen gas was mixed with a stream of 1500 ppm of sulfur dioxide gas. The experimental conditions were the typical bag filter conditions in dry/semi-dry FGD processes. Carbon dioxide and oxygen were not added into the gas mixture because their presence produced little effect on the sulfur dioxide uptake of sorbent at this low temperature[18]. Other gases omitted in the mixture were nitrogen oxides because the current objective is to test the reactivity of the sorbent on sulfur dioxide only. The total flow rate was set at 300 mL/min. At exit, the flue gas composition was continuously monitored by an IMR 2800P flue gas analyzer with readings taken at an interval of 20 seconds.

Prior to fixed bed experiments, the lime was Hydrated, in that, 10 g of it was mixed with 100 mL of either distilled water or 0.1 M of the solution agents and placed in a water bath at 60 °C for 4½ hours. The resulting slurry was filtered and dried in an oven at 100 °C for 16 hours to produce a dry solid. It was then ground, milled and sieved to a particle size of utmost 200 µm before being used in the fixed bed. The reactor was heated to a temperature of 87 °C and a nitrogen gas of 50% humidity ratio was passed through for humidification before the actual sulfation reaction.

The desulphurization activity was monitored through maximum utilization of the sorbent (mol of sulfur dioxide retained/ mol of sorbent) after it was completely exhausted. A blank run was initially tested with glass wool only in the reactor. Afterwards, the sulfation test was run with different hydrated sorbents. Each experiment was done at least twice and the average of the results taken.

The fixed bed results were represented as breakthrough curves where the y-axis was the ratio of current concentration (C) to the inlet concentration ($C_0$) of sulfur dioxide and the x-axis being the time taken. The total sorbent utilization was evaluated from the area difference between the blank run and the reaction curves. The amount of sulfur dioxide retained is given by:

$$\left. mol\ SO_2 retained \middle/ mol\ sorbent \right. = \left(A_{bl} - A_{\exp}\right) C_0 10^{-6} \frac{\varphi_{\upsilon}}{23652} \frac{M_{sorbent}}{m_{sorbent}} \qquad (4)$$

Where $A_{bl}$ is the area under the blank run, $A_{exp}$ is the area under the reaction curve, $C_0$ is the inlet concentration of $SO_2$ (ppm), $\varphi_v$ is the volumetric flow rate (mL/min), 23652 is a volumetric constant depending on the operation conditions, $M_{sorbent}$ is the molar mass of the sorbent used and $m_{sorbent}$ is the mass of the sorbent.

In a bid to explain the results, the hydrated sorbents were prepared for Brunauer-Emmett-Teller (BET) surface area analysis to see the effect of these agents in the surface area and porosity of the sorbents. BJH (Barret, Joyner and Halenda), was applied to obtain the pore-size distribution from nitrogen desorption data. Adsorption measurements were performed on a micrometrics ASAP 2020 Surface Area and Porosity analyzer by the principle of physical adsorption. High purity nitrogen (99.99%) was used. The pore-size distribution is represented by the derivative $d(V_p)/d(d_p)$ as a function of pore diameter, where, $V_p$ is the pore volume and $d_p$ is the pore diameter. Prior to measurement, the samples were degassed and characterized using low temperature (around -197 °C) nitrogen adsorption isotherms measured over a wide range of relative pressures.

To further emphasize the effect of hydrating agents, quantitative and qualitative x-ray diffraction (XRD) analysis using a back loading preparation method was performed for all the hydrated sorbents. The samples were micronized using ethanol and ground for 3 minutes then dried for 24 hours at room temperature. Due to amorphous properties of the materials, 20% of silicon was added to each sample. The dried pellets were ground and properly mixed using motor and pestle before packing them on sample holders. They were analyzed with a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector, variable divergence and receiving slits with Fe filtered Co-Kα radiation in a diffraction angle range (2θ) of 5° to 89°.

Finally Scanning Electron Microscopy (SEM) image scans of the hydrated samples were done to see the effects of the agents on the morphological structure of the quicklime. A LEO 1525 FEGSEM was used for the SEM analysis. The equipment was operated at a vacuum of 2 exp -6 mbar, electron high tension of 1 kV, aperture size of 1 microns, working distance of 7 mm using InLens detector. The imaging was done using Line Integration to reduce noise levels during scanning. The samples were sprinkled onto a double sided carbon tape and placed on aluminum stubs.

## Results and Discussion

Figure 3 shows the reactivity diagrams from pH-stat experiments. The values of the reactivity constant are shown in Table 1. As it can be seen, the value varies according to the additive, the best performing being calcium acetate and deionized water being the least performing. It is clear from this result that all the hydration additives used in this study had a certain positive effect on limes reactivity. This behavior was also observed in the fixed bed (dry FGD) experiments as shown in Figure 4, which shows the breakthrough curves for the sorbents made up from different hydration agents, at 50% relative humidity. From the curves, the capacity of the sorbents to maintain 100% sulfur dioxide removal improved with the hydration agent type. Every agent has its own characteristics which improve the properties of lime thus increasing its reactivity. The amount of sulfur dioxide retained per mol of the sorbent (sorption capacity of the sorbent) is shown in Table 1. As it can be seen, sorbent made from calcium acetate as the agent had the highest amount of sulfur dioxide retained (0.211 mol/mol of sorbent) and sorbent made from water only had the least amount (0.120 mol/mol of sorbent). There is a lot of correlation between these results and the earlier pH-stat results. This shows that in either dry or wet FGD process, the reactivity of the sorbent approximately acts in the same manner. Also these results affirm the observations of Siagi that wet FGD can accurately be simulated by pH-stat method[14].

**Table 1.** Properties of the sorbent varied by type of hydration agent

| Sorbent (Hydration agent used) | Reactivity (x $10^{-4}$ /sec) | Sorption Capacity (mol of $SO_2$/mol of Sorbent) | Surface Area, $m^2/g$ | Average Pore Width (Å) | Amount of $Ca(OH)_2$ formed, % |
|---|---|---|---|---|---|
| Calcium acetate | 2.902 | 0.211 | 3.91 | 159.1 | 65.05 |
| Ammonium acetate | 2.619 | 0.148 | 3.45 | 201.1 | 64.40 |
| Citric acid | 2.558 | 0.141 | 2.90 | 105.2 | 64.14 |
| Water | 2.511 | 0.120 | 1.46 | 131.9 | 60.97 |

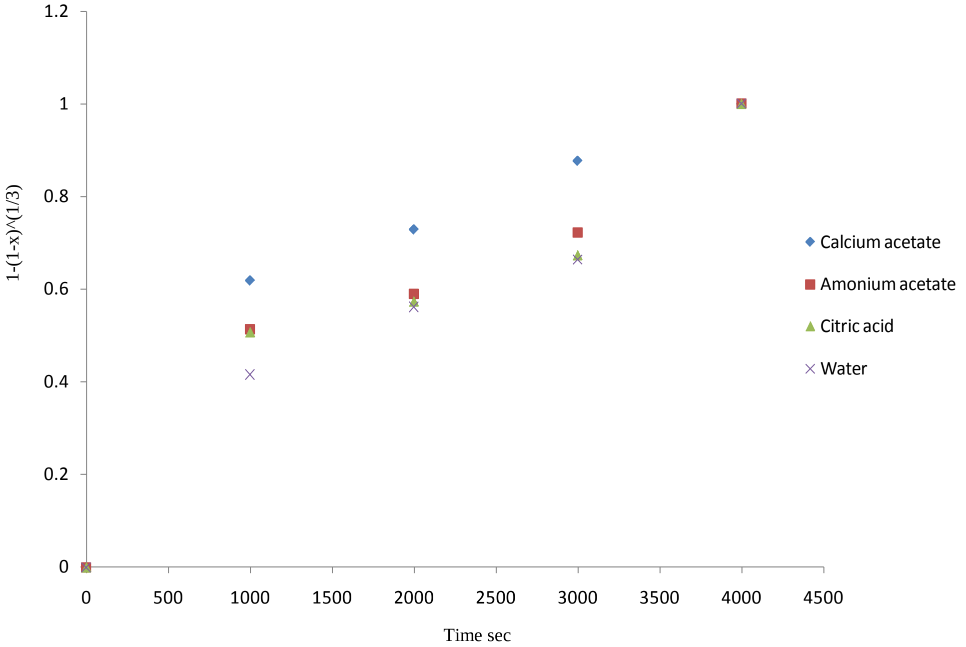


**Figure 3.** Reactivity graphs for different hydration agents

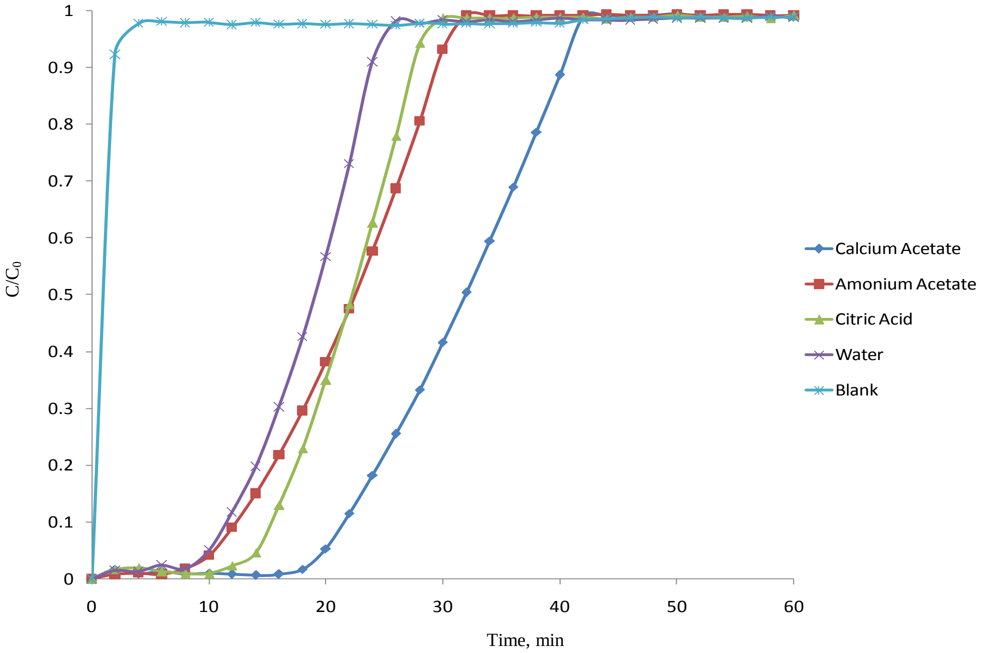


**Figure 4.** Experimental breakthrough curves for sorbents with different hydration agents

The chemical process through which calcium acetate enhances the degree of reactivity can be ascribed to differences in the solubility of the various compounds in the slurry.

Compared to the other agents, calcium acetate will have the highest solubility (therefore it will ionize fully) thus the largest augmentation[19]. The increase is thus possible due to higher concentration of calcium ions in the solution which precipitate out as $Ca(OH)_2$ through common ion effect and thus improvement in reaction. The presence of $Ca^{2+}$ ions accelerates the rate of reaction[20]. A proposed mechanism which can lead to addition of lime reactivity when calcium acetate is used as the hydration agent can be: the agent particles first dissolve to give calcium-acetate complex ions, the complex ion then migrates away from the mother particle to give a precipitate of calcium hydroxide in the bulk of the solution. The hydroxide being formed is the main reactive compound, thus, the more it is formed, the higher the reaction[21]. The acetate ions play a crucial role in enhancing the degree of reactivity possibly due to its relatively strong complexation power[22].

The increase in the amount of slaked lime produced when calcium acetate is the hydrating agent can also be explained by the hydrolysis of the acetate ion[21]. A possible mechanism is given below:

- Ionization of calcium acetate:

$$Ca(CH_3COO)_2(aq) \rightarrow Ca^{2+}(aq) + 2CH_3COO^{-}(aq) \quad (5)$$

  Where additional $Ca^{2+}$ ions are formed.

- Hydrolysis of the acetate ion takes place:

$$2CH_3COO^{-}(aq)+2H_2O(l) \rightarrow CH_3COOH(aq) + 2OH^{-}(aq) \quad (6)$$

  Where more $OH^{-}$ ions are generated.

- The $OH^{-}$ ions are moved from solution by $Ca^{2+}$ to form $Ca(OH)_2$:

$$Ca^{2+}(aq) + 2OH^{-}(aq) \rightarrow Ca(OH)_2(s) \quad (7)$$

- The acetic acid then reacts with CaO to form $Ca(CH_3COO)_2$ and the above series of reactions takes place, over and over, each cycle leading to more production of $Ca(OH)_2$.

Consequently, the total slaked lime formed when calcium acetate is used as a hydrating agent comes from two sources:

a) From the hydrolysis of the acetate and the subsequent reaction of $OH^{-}$ ions with $Ca^{2+}$ and

b) From the reaction of acetic acid with CaO to produce fresh $Ca(CH_3COO)_2$.

The increase in reactivity of sorbents formed by solution of ammonium acetate ($NH_4CH_3COO$) can also be explained by an increase in the amount of slaked lime caused by hydrolysis reaction. After ionization of ($NH_4CH_3COO$), the $NH4^+$ ion may also undergo hydrolysis:

$$NH_4^+(aq) + H_2O(l) \rightarrow NH_3(aq) + H_3O^+(aq) \quad (8)$$

The $H_3O^+$ formed from reaction (eq. 8) can then increase the dissolution of CaO to form more $Ca^{2+}$ through:

$$H_3O^+(aq) \rightarrow H^+(aq) + H_2O(l) \quad (9)$$

$$CaO(s) \rightarrow Ca^{2+}(aq) + O^{2-}(aq) \quad (10)$$

$$2H^+(aq) + O^{2-}(aq) \rightarrow H_2O(l) \quad (11)$$

As the ammonium ionizes, additional $H^+$ is provided by reaction (eq. 9), which causes more quicklime to dissolve - reaction (eq. 10), since it is consumed by reaction (eq. 11), thereby increasing the quicklime dissolution. The acetate ion on the other hand undergoes hydrolysis as explained in reactions (eq. 6) above[4].

Quicklime swell when exposed to a vapor of acid-water thus increase in its surface area[3]. Though the enhanced degree of reactivity for the hydrations performed in the acidic hydrating agent (citric acid) seems to be due to the higher concentration of $H^+$ ions in the solution, by increasing the solubility of quicklime through the following reaction:

$$CaO(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) \qquad (12)$$

Reactions between citric acid and quick[21] lime can also be a good source of $H^+$. These reactions are dependent upon the solubility of quick lime in the hydrating agent solution. The more the solubility, the higher the reactivity of the product[23]. This solubility is also thought to affect the pH of the resulting product and therefore the reaction as a whole. At pH values below 11.5, the rate-determining step is $OH^-$ adsorption followed by $Ca^{2+}$ and $OH^-$ desorption leading to a rate maximum. Reaction (ix) below describes the overall dissolution process at pH values below 11.5.

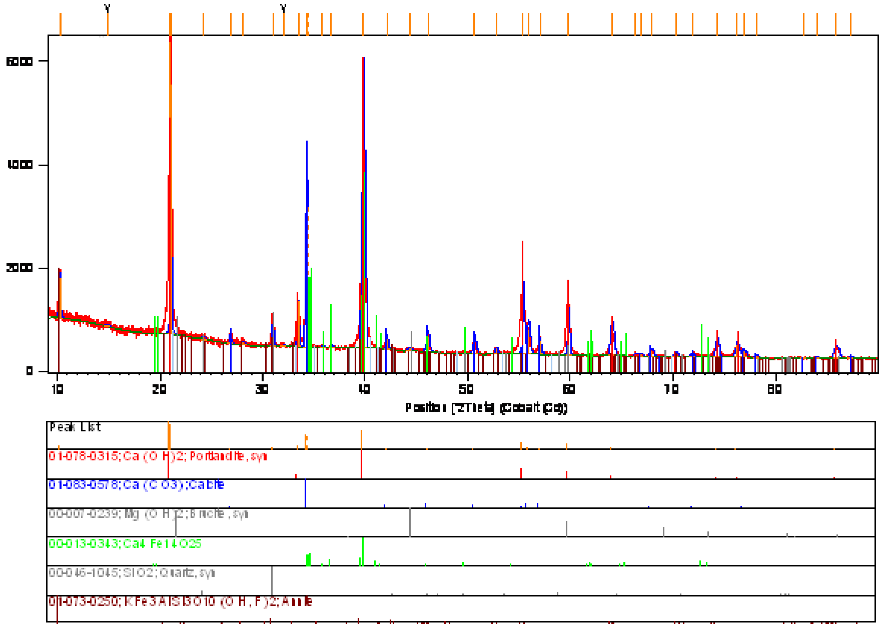
$$CaOH^+(surface) + OH^- \rightarrow CaOH^+.OH^-(surface) \rightarrow Ca^{2+}(aq) + 2OH^-(solution) \qquad (13)$$

The $OH^-$ ions adsorptions followed by the $Ca^{2+}$ ions desorption are critical steps in dissolving quick lime in solution at pH values below 11.5. The degree of hydration thus formation of slacked lime, greatly decreases in strong basic regions due to a lower quicklime solubility and lower amount of $OH^-$ ions produced[24]. A decrease in pH results in a high dissolution rate whereas a low dissolution rate can be attributed to a high pH. This explains the improvement of reactivity when citric acid was used. Also as indicated in reaction (eq. 6), the agents containing acetate ions produced acetic acid with a net effect of reduction in pH thus improved dissolution and reactivity as a whole.

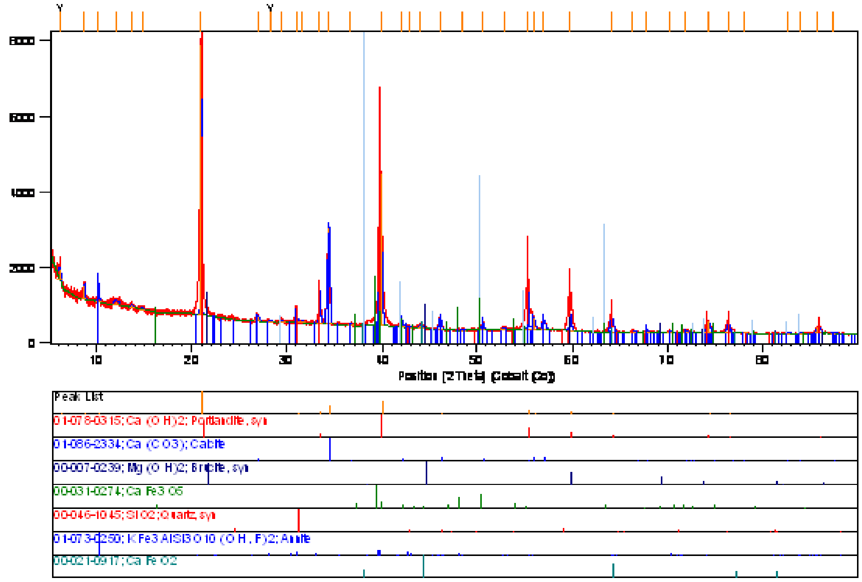
Table 1 further show the variation of surface area with the type of hydrating agent used. The increase in surface area of the sorbents formed might either be by the virtue of the amount of slaked lime formed or it might be by the virtue of the morphology of the slaked lime formed. This necessitated XRD analysis and SEM image scanning of the formed sorbents to be performed. The increase in reactivity of the sorbents formed is largely attributed to the increase in surface area. This is observed in the relation between the reactivity, sorption capacity and surface area in Table 1. In addition, the highly reactive sorbents had very low *t*-plot values and pore size range of between 105 – 202 Å as indicated in Table 1, which is evidence that the pore size were in the mesopore region according to International Union of Pure and Applied Chemistry (IUPAC). As stated in literature, this is the effective zone for FGD process[25].

Rapid hydration of quick lime will result in the formation of relatively big hydroxide aggregates consisting of submicroscopic crystallites with high surface area-particle morphology[22]. If the products were formed at a high rate, the possibility of crystal formation is reduced, thus smaller, high surface area slacked lime particles are formed instead[26]. Still, carboxylic salts of calcium are known to form high-porosity cenospheric particles upon devolatilization of their organic compounds. These cenospheres provide large internal surface area and impose minimal mass diffusion limitations to heterogeneous reactions with $SO_2$. The physical structure of the cenospheres formed upon devolatilization is influenced by each sorbent's chemical composition. As the weight percent of organic hydrocarbons in the sorbent molecule increases, pore surface area and total pore volume of the cenospheres also increase. Physically, as a greater amount of volatiles are bubbled through the matrix, total surface area within the cenosphere is increased[2].

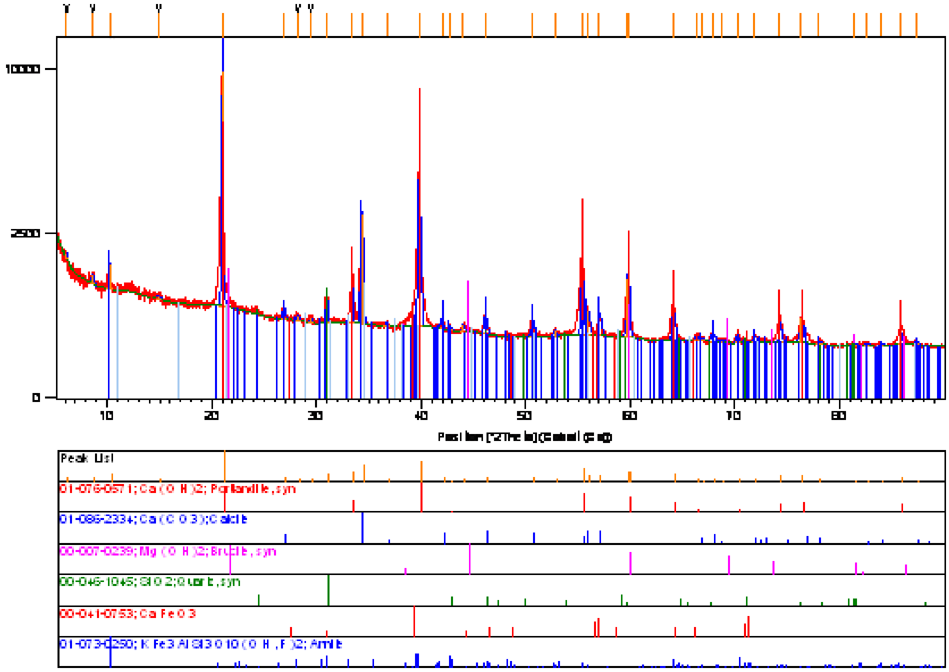
XRD spectra of the hydrated sorbents are shown in Figure 5 above. It is from this qualitative and quantitative XRD analysis that the respective amount of slacked lime in the sorbents was obtained as indicated in Table 1. Slacked lime and uncalcined calcite are the main reactive compounds in these sorbents. As it can be seen in the spectra, most of the quick lime was converted to slacked lime, depending on the hydration agent used, with an optimum amount of slacked lime being formed when calcium acetate is used as an agent.



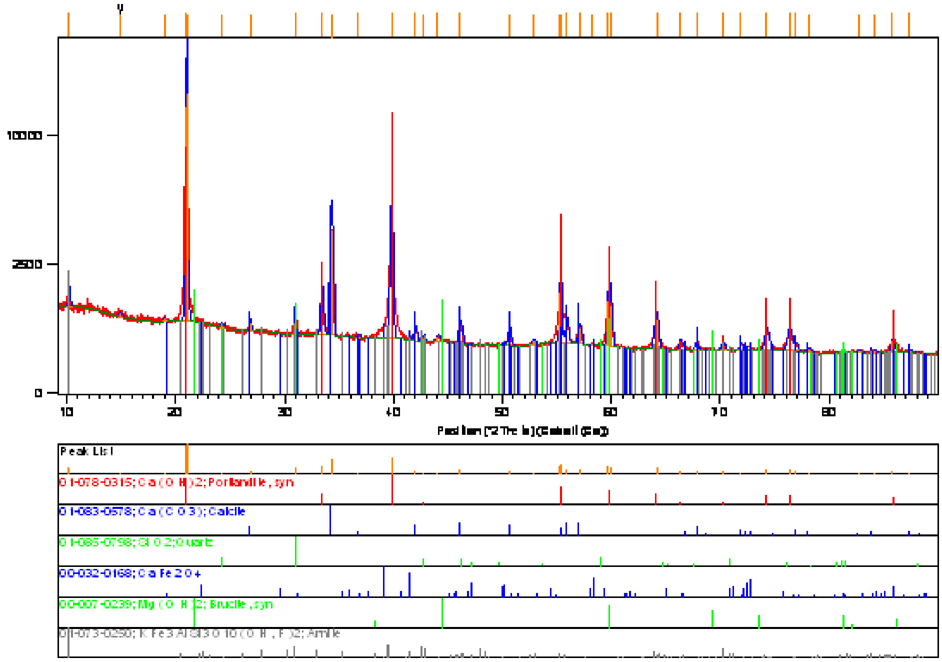
a) Calcium acetate



b) Ammonium acetate



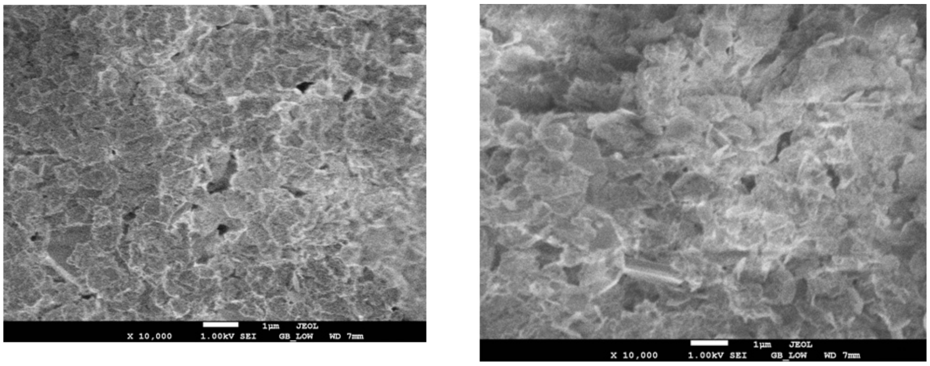
c) Citric acid



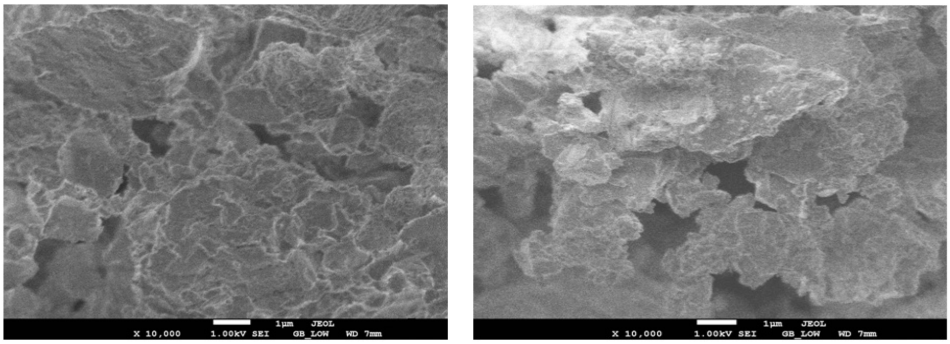
d) Water

**Figure 5**. XRD spectra of sorbents made from respective hydration agent

Figure 6 shows the SEM images of the sorbents by the virtue of the hydrating agent used. Various levels of brightness indicate difference in the surface chemistry. Figure 6 (a), (b) and (c) shows irregular, coarse and rough surface morphologies which indicate that the hydrating agents create a porous structure. The enhanced surface area of the sorbents made from hydrating agents may also be attributed to the increased roughness of the structure. When water alone is used, the morphology is somehow rough with Figure 6 (d) showing a structure with small pores and cracks, The physical and chemical changes in the sorbent as it was prepared were the cause of this final structural morphology.



a) Calcium acetate b) Ammonium acetate



c) Citric acid d) Water

**Figure 6.** SEM images of sorbents made from respective hydration agent.

## Conclusion

Calcite was calcined into quick lime, and then hydrated to slacked lime. Various hydration agents, namely; calcium acetate, ammonium acetate and citric acid were compared to pure distilled water in terms of the reactivity of the sorbent produced through either a pH-stat method that simulate wet flue gas desulfurization or fixed bed apparatus for dry desulfurization. BET surface area analysis, x-ray diffraction and SEM imaging were used to explain the results. All hydration agents improved lime's reactivity, the best agent being calcium acetate, followed by ammonium acetate. Hydrolysis and dissolution were thought to be the cause of the observed results. For future studies, it is recommended that these agents be used with pozzolanic materials because recent research has it that lime reactivity is highly improved when mixed with pozzolanic materials. Also, application of these agents in removal of both $NO_x$ and $SO_2$ can form an interesting future topic.

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