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MODELLING AND EXPERIMENTAL MEASUREMENTS OF LIMESTONE DISSOLUTION UNDER ENHANCED WET LIMESTONE FGD PROCESS CONDITIONS*

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Abstract

The influence of ammonium sulphate additive to the solution in the wet flue gas desulphurization (FGD) process performance has been experimentally determined and modelled. It was observed that the buffer capacity of the solution could be increased by up to 500 %. The experimental results on the limestone dissolution rate in a pH stated apparatus are reported under various relevant parameters (concentrations of ammonium and chloride ions, pH value and temperature). The results are reported as a linear dissolution rate ($\mu m\ s^{-1}$) and are particle size independent. It was found that the performance of the ammonium ion is comparable to that of adipic acid, which is a well-known additive in FGD applications. Both additives increase the buffer capacity of the solution and the limestone dissolution rate.

Introduction

The wet limestone process is commonly used for the desulphurization of flue gas from coal-fired power stations. In this process, the SO_2 from the flue gas is absorbed in a spray tower by limestone/gypsum slurry with a temperature of about 60 °C. The SO_2 absorbed is neutralised with limestone ($CaCO_3$) and oxidised to sulphate with sparged air in a make-up tank. The product of the process is gypsum ($CaSO_4.2H_2O$). The factors determining the size of the equipment and the consumption of energy used for the

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* Dedicated to the memory of Prof. Dr. Jože Šiftar

process operation are the absorption capacity of the slurry sprayed into the scrubber, the rate of oxidation of the sulphite, and the rate of limestone dissolution in the make-up tank.

Possible optimisation of the process can normally be performed in two directions:

- Improvements in the absorber. It is possible to use a more efficient type of absorber (e.g. a spray absorber with packing, venturi absorber, falling film absorber, etc.), or to improve the local aero- and hydro- dynamical conditions in the absorber [1-4]. However, these can result in other adverse impacts such as creating areas of potential plugging and scaling.
- Improvements in the chemistry of the process. It is possible to use additives which improve the absorption (buffer) capacity of the slurry and the limestone dissolution rate. Organic acids (e.g. adipic acid) are industrially-proven additives; ammonium salts, however, represent an innovation proposed by General Electric, Environmental Services, Inc. [5].

In this paper, the modelling and experimental measurements of the influences of various additives on the buffer capacity to absorb slurry and limestone dissolution will be discussed. The effects of ammonium sulphate as an additive on the operation of a pilot plant are reported in [5].

Modelling

The objectives of the research and modelling were as follows:

- The effect of ammonium sulphate additive on the equilibrium composition of the relevant ions in the absorbing slurry and
- The influence of NH_4^+ ions in the solution on the buffer capacity.

Our goal was to model the buffer capacity to absorption slurry at pH value change ($\Delta pH = pH_{input} - pH_{output}$) in the absorber tower. The slurry is acidified from input pH (in the neutralisation tank) to a certain pH value at the absorber output. The modelled buffer capacity was correlated with the required L/G volume ratio in the absorber at a given constant output SO_2 concentration.

The following relevant equilibrium reactions were considered in modelling: dissociation of dissolved SO_2 (sulphite), sulphate, carbonate, ammonium, water and ammonium carbonate, solubility products of $CaCO_3$ and $CaSO_4.2H_2O$, and CO_2 gas solubility in water.

The relevant chemical reactions and equilibrium equations can be expressed as follows:

$$H_2SO_3 + H_2O \leftrightarrow H_3O^+ + HSO_3^- \qquad K^1_{H_2SO_3} = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]} \tag{1}$$

$$HSO_3^- + H_2O \leftrightarrow H_3O^+ + SO_3^{2-} \qquad K^2_{H_2SO_3} = \frac{[H_3O^+][SO_3^{2-}]}{[HSO_3^-]} \tag{2}$$

$$H_2SO_4 + H_2O \leftrightarrow H_3O^+ + HSO_4^- \qquad K^1_{H_2SO_4} = \frac{[H_3O^+][HSO_4^-]}{[H_2SO_4]} \tag{3}$$

$$HSO_4^- + H_2O \leftrightarrow H_3O^+ + SO_4^{2-} \qquad K^2_{H_2SO_4} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} \tag{4}$$

$$H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^- \qquad K^1_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} \tag{5}$$

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \qquad K^2_{H_2CO_3} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} \tag{6}$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad K_{NH_3} = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{7}$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \qquad K_{H_2O} = [H_3O^+][OH^-] \tag{8}$$

$$NH_4HCO_3 \leftrightarrow NH_4^+ + HCO_3^- \qquad K_{NH_4HCO_3} = \frac{[HCO_3^-][NH_4^+]}{[NH_4HCO_3]} \tag{9}$$

$$NH_4CO_3^- \leftrightarrow CO_3^{2-} + NH_4^+ \qquad K_{NH_4CO_3^-} = \frac{[CO_3^{2-}][NH_4^+]}{[NH_4CO_3^-]} \tag{10}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4.2H_2O \qquad K_{sp,\,CaSO_4} = [Ca^{2+}][SO_4^{2-}] \tag{11}$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \qquad K_{sp,\,CaCO_3} = [Ca^{2+}][CO_3^{2-}] \tag{12}$$

$$K_{H,\,CO_2} = p_{CO_2} \cdot c_{H_2CO_3} \tag{13}$$

It should be noted that under the given conditions (pH < 6), the conversion of NH_3 and CO_2 to carbamate anion had a negligible effect and was not considered.

The equilibrium constants at the given temperature (60 °C) were calculated from thermodynamic data prepared by Brewer [6].

The electroneutrality of the solution was also considered. In addition, the chloride anion (Cl^-) was considered, as it is subject to accumulation in the absorbing solution due to the presence of HCl in the flue gas.

$$\sum_{i=1}^{i=n} z_i c_i = 0 \tag{14}$$

In equation 14 z_i and c_i represent, for the given ion i, the electrical charge (including sign) and the concentration, respectively, n is the number of all ions considered.

The activity was considered using activity coefficients according to the adapted Pitzer/Hebye/Hueckel equation [7].

The overall mass balance (concentration) for the carbonate, sulphite and sulphate species was calculated as *CT*, *S4T* and *S6T*, respectively:

$$CT = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [NH_4HCO_3] + [NH_4CO_3^-] \tag{15}$$

$$S4T = [H_2SO_3] + [HSO_3^-] + [SO_3^{2-}] \tag{16}$$

$$S6T = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}] \tag{17}$$

The system of 17 equations and 17 variables was solved numerically. A computer program was developed to perform calculations.

The calculation procedure was performed in three steps:

- First, for a given total NH_4^+/NH_3 concentration and for a given Cl^- concentration, the concentrations were calculated considering the equilibrium with both solid phases (limestone and gypsum). The results were used in the second step.
- In the second step the solid phases were “removed”. The equilibrium between solution and the solid phase was no longer considered in the calculations. The solution contained equilibrium concentrations of ions and had a pH value of about 7. Then, the solution was acidified by increasing the Cl^- concentration, and the new equilibrium concentrations and the pH value were calculated. This was performed until a given pH value (observed in the pilot plant slurry conditioning tank as pH input) was reached. The corresponding Cl^- concentration was then stored. The model acidification with Cl^- ions was used to simulate a standard analytical procedure for dissolved carbonate determination, which is carried out by the titration with the HCl solution.

- In the third step the solution was further acidified by increasing the Cl^- concentration until the pH value reached the measured value of absorbing slurry at the output of the spray absorber (pH output). The final Cl^- concentration was compared to the stored value from the second step of the calculations and the difference was used as the expression for the buffer capacity (Δc_{Cl-} in mol L^{-1}) under the given input conditions mentioned in step one.

Modelling results

The pilot plant operation data were used in the modelling of the absorbing slurry buffer capacity. The pilot plant was connected to unit 5 at the Šoštanj coal-fired power station, Slovenia. The pilot plant data on the chemical composition of absorbing slurry (concentration of NH_4^+, Cl^- ions, total concentration of sulphite, sulphate and carbonate species) and the pH value in the neutralisation tank (absorber input) and at the absorber output were used. Consequently, the data on the required L/G volume ratio in the spray absorber to reach the prescribed emission mass concentration of SO_2 at the absorber output of 400 mg m^{-3} (at normal conditions) were also used. The other data on pilot plant operation using additives are reported in [5].

The input data for model calculations, the required L/G volume ratio in the absorber and the model results are presented in Table 1. The pilot plant had the following process parameters: input flue gas flow rate 12,000 m^3 h^{-1} (at normal conditions), input SO_2 mass concentration in flue gas 4,500 mg m^{-3} (at normal conditions), absorbing slurry temperature 60 °C.

The results from Table 1 are presented in Figures 1 and 2. The effect of ammonium concentration on the required L/G ratio in the absorber (pilot plant data) and on model solution buffer capacity (Δc_{Cl-}) are presented for input pH at 5.8 and 5.3 at zero Cl^- concentration (in the pilot plant).

It can be observed that the introduction of the ammonium ion does increase the buffer capacity to absorb slurry and that this increase corresponds to a change (decrease) in the required L/G ratio for the same absorber performance. The increased buffer capacity is caused by the increased concentration of the HCO_3^- ion as calculated in model procedure step one.

Table 1 : Pilot plant data used in model calculations and model results expressed as required increased concentration of Cl^- anion to change input pH to output pH.

pilot plant data					model result
pH (input)	pH (output)	c_{NH4+} (g L^{-1})	c_{Cl-} (g L^{-1})	L/G (L m^{-3})	Δc_{Cl-} (mol L^{-1})
5.80	4.71	0	0	14.5	$2.2 . 10^{-3}$
5.98	3.95	3	0	11.8	$8.8 . 10^{-3}$
5.66	3.86	5	0	11.4	$7.6 . 10^{-3}$
5.66	3.86	8	0	10.4	$9.9 . 10^{-3}$
5.76	4.14	5	20	13.5	$2.8 . 10^{-3}$
5.85	4.81	5	40	14.5	$2.6 . 10^{-3}$
5.77	4.83	8	40	11.8	$2.6 . 10^{-3}$
5.58	4.30	0	0	15.0	$1.6 . 10^{-3}$
5.47	3.93	2	0	14.1	$3.4 . 10^{-3}$
5.17	3.67	5	0	14.0	$4.4 . 10^{-3}$
5.23	3.34	5	20	18.0	$1.7 . 10^{-3}$
5.27	3.90	5	40	26.4	$1.2 . 10^{-3}$

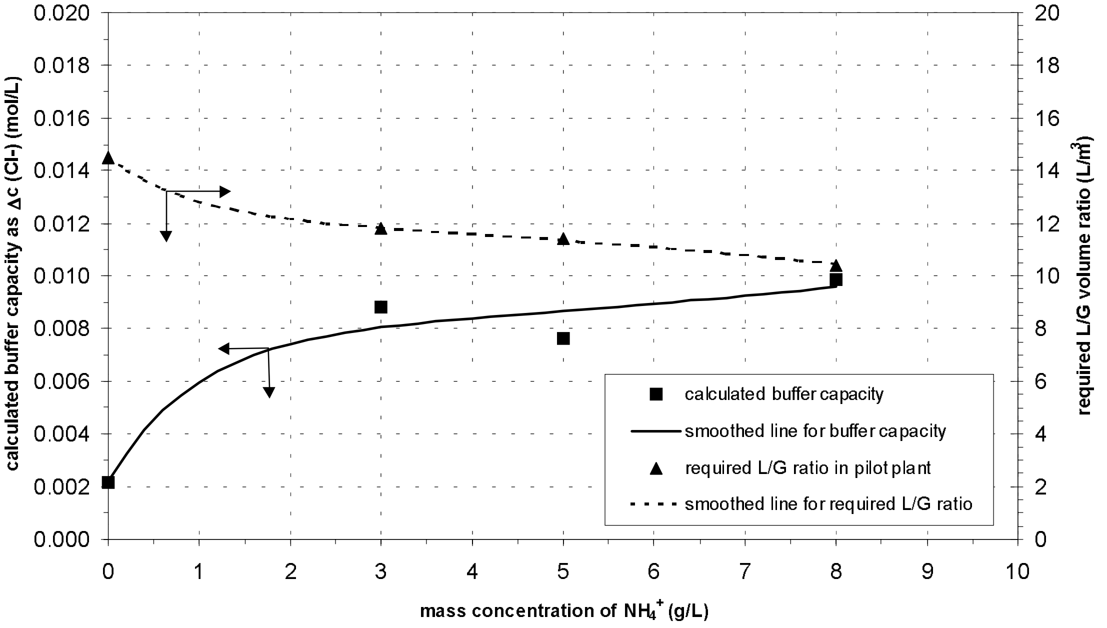

Figure 1: The effect of ammonium concentration on required L/G ratio in pilot plant and on calculated buffer capacity of absorbing slurry in absorber (at pH 5.8).

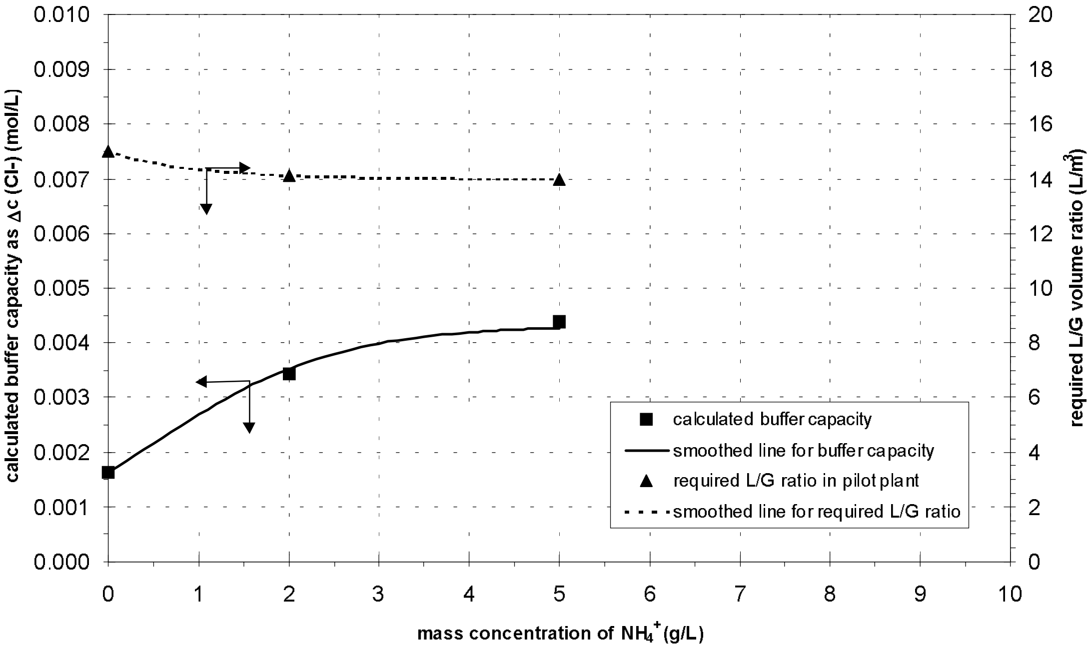

Figure 2: The effect of ammonium concentration on the required L/G ratio in pilot plant and on calculated buffer capacity of absorbing slurry in absorber (at pH 5.3).

Experimental work

In the experimental work the influence of ammonium sulphate on the limestone dissolution rate was determined in a pH-stated apparatus. This technique has already been reported in the literature [8, 9]. The previously reported methods and results [9] have now been expanded to determine the effect of the introduced ammonium ion to the limestone slurry. The ammonium ion increases the buffering capacity of the solution and consequently promotes the dissolution rate of limestone particles. In contrast, the accumulated chloride ions in the solution inhibit the promoting effect of ammonium ions. Thus, the effect of the ammonium and chloride ions concentration in the bulk of the test solution (limestone slurry) was the subject of measurements in pH-stated apparatus under controlled conditions.

Tests were carried out under the following experimental conditions:

- The apparatus reported in [9] was used. The volume of test solution was 1 L.
- Vigorous stirring was applied by 50 mm turbine stirrer at 720 min^{-1}.

- In all tests commercial ground limestone from the Kamnik stone quarry (used in industrial FGD plant unit 4 at the Šoštanj power plant, Slovenia) was used. The size distribution of limestone particles is presented in Figure 3. The initial amount of limestone introduced to the apparatus was 2.00 g per liter of solution.
- 0.5 mol L^{-1} HCl solution was used to maintain a constant pH value during the test.
- Test solutions with various concentrations of ammonium and chloride ions were prepared in the same apparatus from distilled water, $(NH_4)_2SO_4$ and $CaCl_2$ (p.a. quality chemicals were used). After the introduction of chemicals, the precipitation of gypsum occurred. The ranges of ammonium and chloride ion mass concentrations in the test solutions were 0 to 20 g L^{-1} and 0 to 71 g L^{-1}, respectively.
- The pH values of 5.0, 5.5 and 5.8 were maintained.
- The temperature of the slurry was maintained at 20 °C or 60 °C.
- The solution was sparged with air at 120 L h^{-1} in order to remove the liberated CO_2.

The experiment was controlled by a computer that performed the pH measurement, and the regulation and control of the amount of acid solution introduced into the apparatus over the time. The result of the experiment was the time dependence of the amount of undissolved limestone. The dimensionless quotient of limestone mass at a given time by initial limestone mass was introduced, and will be referred to as *F*.

$$F_{(t)} = \frac{m_{(t)}}{m_{(0)}} \tag{18}$$

A model of limestone dissolution in a pH-stated apparatus [9] was used to correlate the dependence of *F* against time *t* and given polydispersed limestone granulation data (Figure 3) to linear dissolution rate under the given experimental conditions (chemical composition in bulk of solution). Linear dissolution rate (k_{dis} in µm s^{-1}) will be used as the final result of the experimental work.

The linear dissolution rate was obtained in the following way. The data on polydisperse limestone particle size distribution was arranged to a set of monodisperse particle sizes, considering the particles as spheres. The value of k_{dis} was arbitrarily chosen, and the dissolution of each particle size in a set was calculated in a small time interval. The reduction of particle(s) diameter was considered in the next iteration. Thus, a model dependence of calculated *F* against time was obtained. By comparison of experimental and model calculated curves, the best-fit value of k_{dis} was found by trial and error for each experiment. An example of the experimental and model calculated curves of *F* against time is presented in Figure 4.

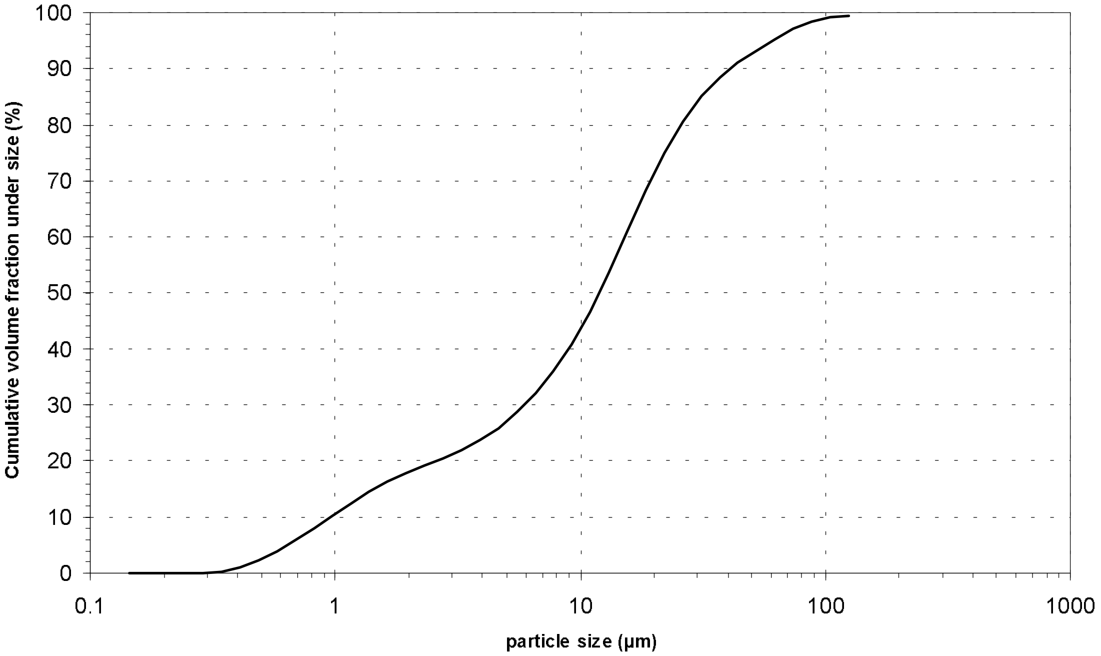

Figure 3: Particle size distribution for commercial limestone (from Kamnik stone pit) used in the experimetal work.

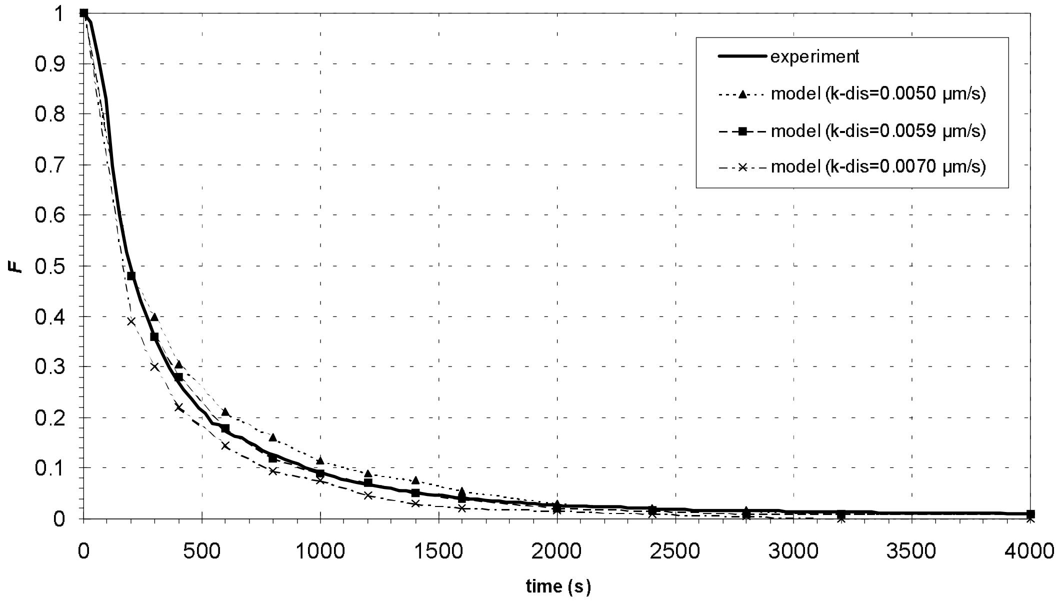

Figure 4: Example of model calculation of k_{dis} from experimental *F* against time curve by guessing (trial and error). Value of 0.0059 μm s^{-1} was used in this example as the best fit (at 60 °C, pH 5.8, 10 g L^{-1} NH_4^+ and 7.1 g L^{-1} Cl^-).

It was estimated that the maximum overall error of measurement and calculation of k_{dis} was up to ± 30 %.

Experimental results

The majority of experimental measurements were performed at pH=5.8 and 60 °C. The effect of the ammonium and chloride ions in bulk of test solution will be presented, as well as comparisons with other cations and other ammonium salts. The effect of additives on the limestone dissolution rate will be given as the calculated k_{dis} or as the experimental curve F versus time.

The effect of ammonium ion bulk mass concentration on k_{dis} at three pH values (5.8, 5.5, 5.0), at 60 °C and for 7.1 g L^{-1} Cl^- mass concentration is presented in Figure 5. For higher chloride concentration, the effect is presented in Figures 6 and 7 (at 35.5 and 71 g L^{-1} Cl^-, respectively).

The effect of temperature on k_{dis} at different ammonium ion concentrations is presented in Figures 8 and 9 (at pH 5.8 and 5.0, respectively, and at 7.1 g L^{-1} Cl^- concentration).

Various other additives were also tested. Magnesium, potassium and sodium sulphates were used at mass concentrations equivalent to that of ammonium sulphate (0.28 mol L^{-1} sulphate mass concentration was used as the reference value). For comparison, no additive at all and the well-known additive adipic acid at mass concentration of 1 g L^{-1} , were also tested. The comparison is given as F against time curves in Figure 10 (at 60°C and pH 5.8).

It can be concluded from the results, that cations like Mg^{2+}, K^+ and Na^+ do not promote limestone dissolution and only adipic acid has a comparable effect on the ammonium ion.

The comparison of ammonium salts (NH_4Cl, NH_4NO_3) as additives to $(NH_4)_2SO_4$ is presented in Figure 11 (the curve with no ammonia added is also shown). Comparison is given at 60 °C, pH 5.8, 10 g L^{-1} $NH4^+$ (0.58 mol L^{-1}) and 7.1 g L^{-1} Cl^-. We can conclude that the choice of ammonium salt has no influence.

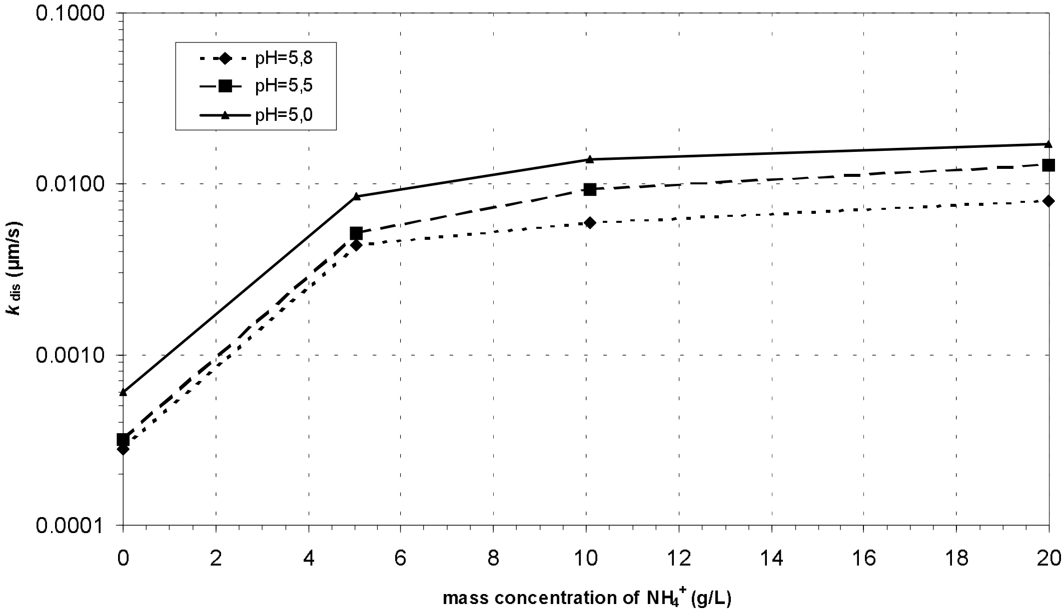

Figure 5: Comparison of ammonium ion mass concentration effect on k_{dis} at three pH values (at 60 °C and 7.1 g L^{-1} Cl^{-}).

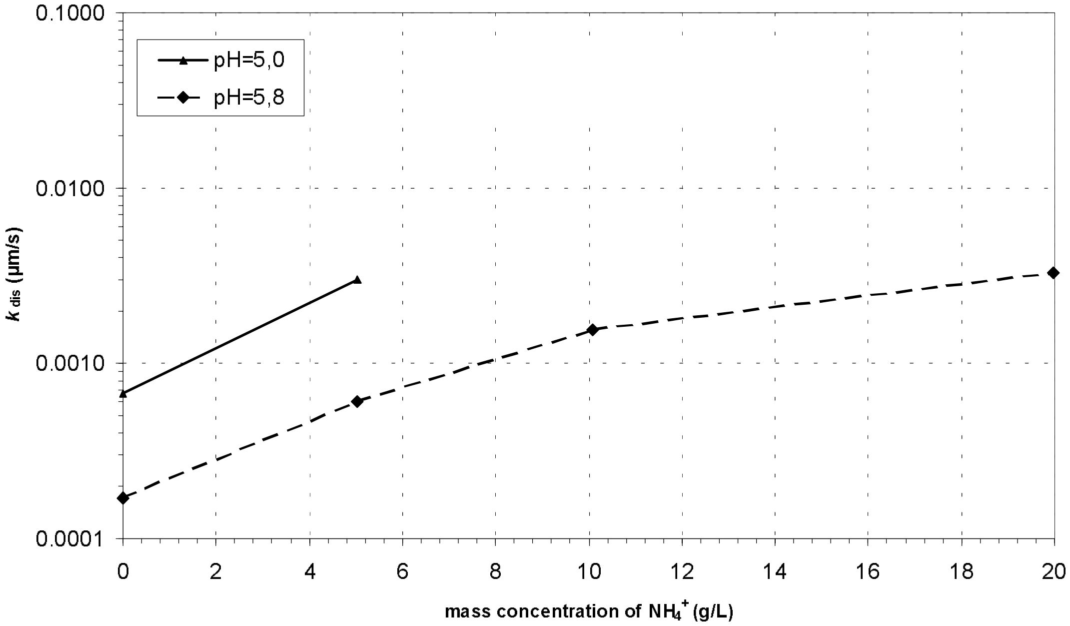

Figure 6: Comparison of ammonium ion mass concentration effect on k_{dis} at three pH values (at 60 °C and 35.5 g L^{-1} Cl^{-}).

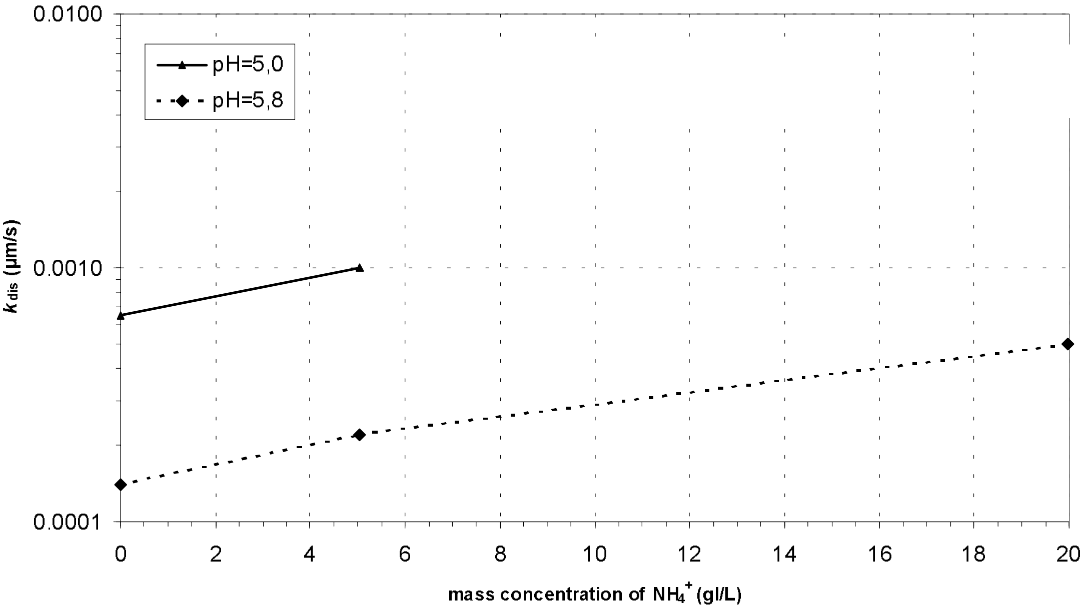

Figure 7: Comparison of ammonium ion mass concentration effect on k_{dis} at three pH values (at 60 °C and 71 g L^{-1} Cl^-).

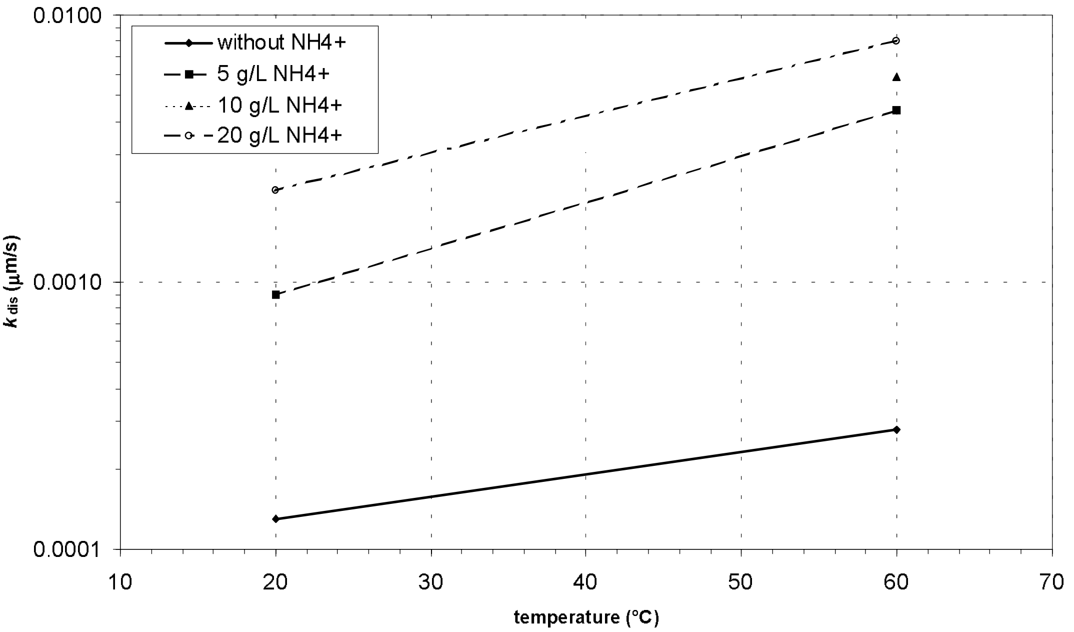

Figure 8: Comparison of temperature effect on k_{dis} at various ammonium ion mass concentrations (at pH 5.8 and 7.1 g L^{-1} Cl^-).

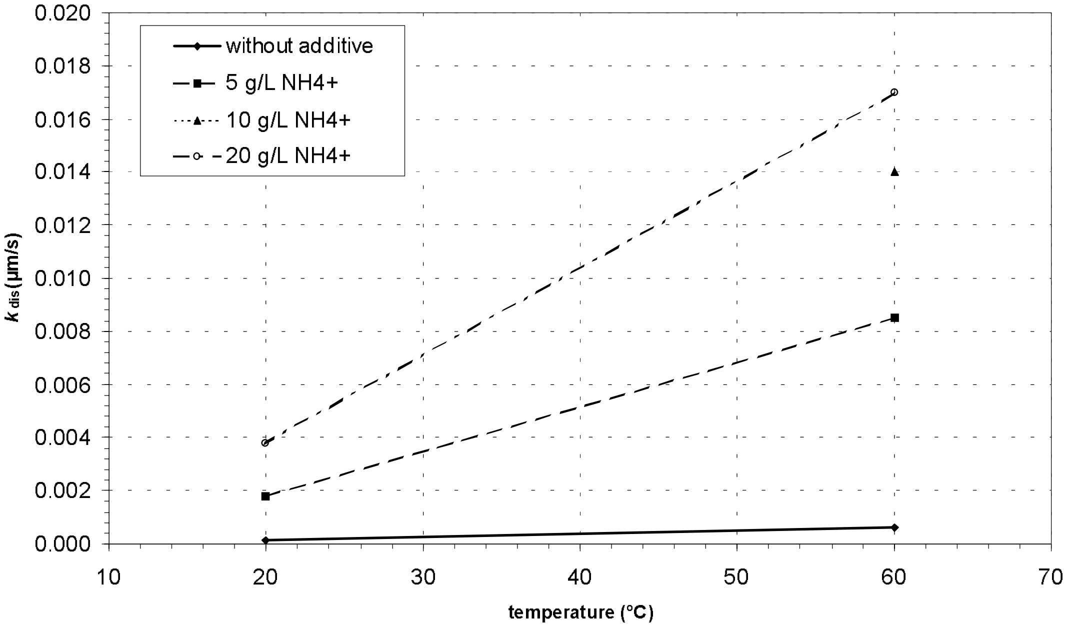

Figure 9: Comparison of temperature effect on k_{dis} at various ammonium ion concentrations (at pH 5.0 and 7.1 g L^{-1} Cl^{-}).

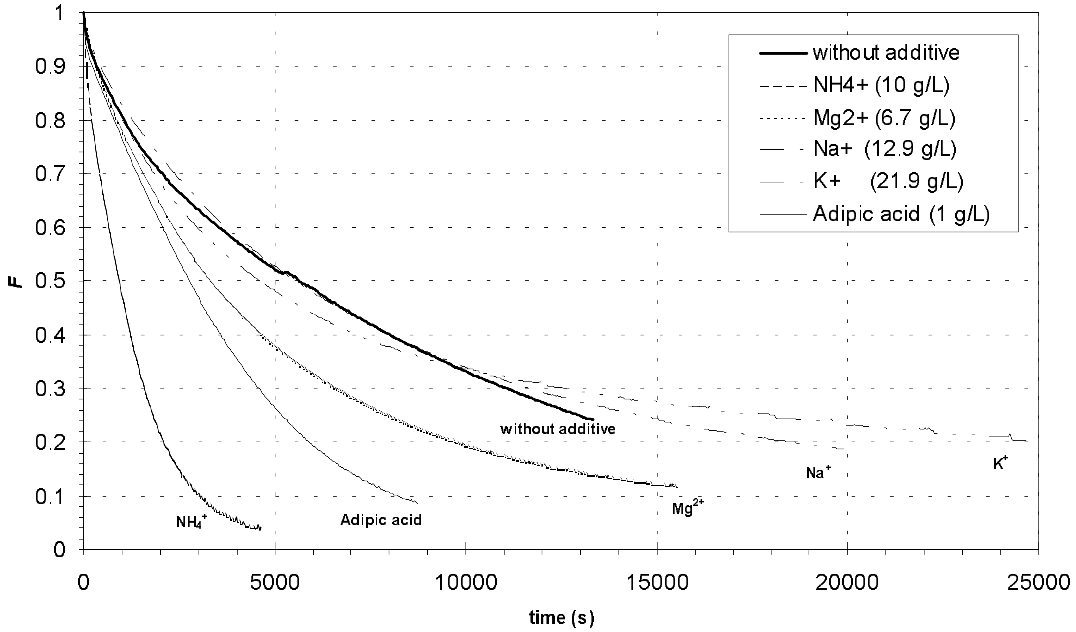

Figure 10: Comparison of Mg^{2+}, K^{+} and Na^{+} cations (as sulphates) to NH_4^{+} on limestone dissolution curve of *F* against time. Curves for absence of additives and for adipic acid are also shown (conditions: 60 °C, pH 5.8 and 35.5 g L^{-1} Cl^{-}).

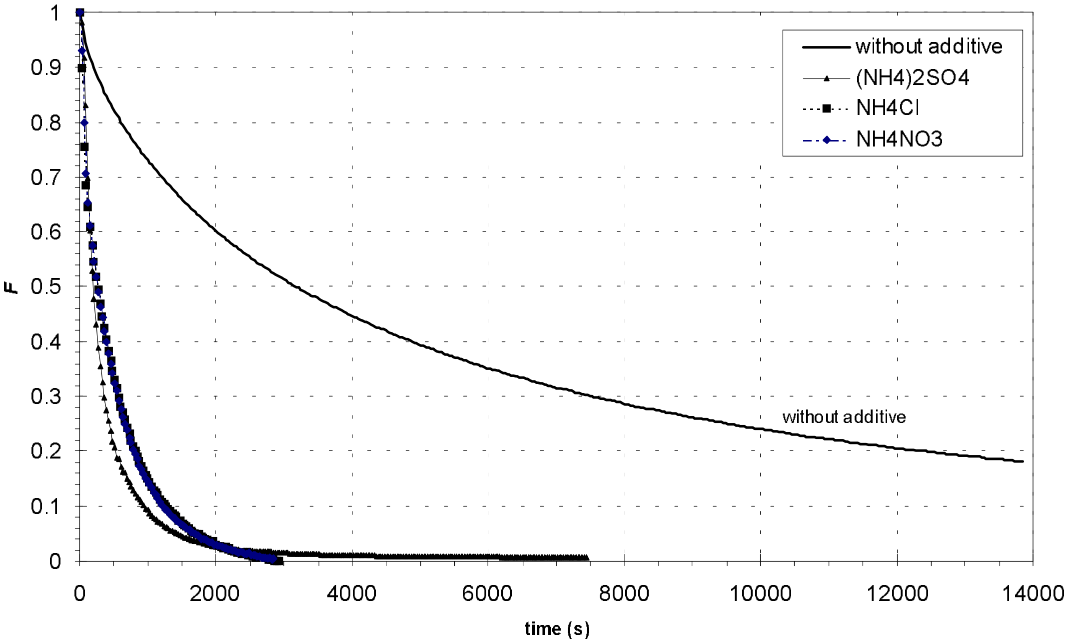

Figure 11: Comparison of various ammonium salts effect on limestone dissolution rate (conditions: 60 °C, pH 5.8, 10 g L^{-1} NH_4^+, 7.1 g L^{-1} Cl^-).

Conclusion

Experimental results show that the introduction of ammonium ions significantly increases the buffer capacity of the absorbing slurry. According to the modelling of solution equilibrium, the cause is the increased concentration of the HCO_3^- ion due to high NH_4^+ ion concentration. A small contribution (up to 10 % of overall concentration for all CO_2 species) also results from the association of NH_4^+ and HCO_3^- ions to $NH_4HCO_3^0$ and $NH_4CO_3^-$ in the solution. The calculations of the buffer capacity in the spray absorber showed that the buffer capacity between the input pH value (e.g. 5.8) and the output pH value (3.3 to 4.9) could be up to 500 % higher. However, the required L/G volume ratio in the absorber is only reduced by up to 30 % [5], as a result of other resistances to the mass transfer in the absorber [2].

Experimental measurements of limestone dissolution in the pH stated apparatus show that the introduced ammonium ion significantly promotes the dissolution rate. The linear dissolution rate, k_{dis}, can be increased by up to 30 times. The quantitative influences of all relevant parameters (pH, temperature, ammonium and chloride ion concentrations) are also presented graphically. The results are independent of limestone particle size distribution and are useful for the modelling of given limestone dissolution in industrial scale FGD plant.

It is also shown that other cations (Mg^{2+}, K^+, Na^+) do not influence limestone dissolution. Three ammonium salts ($(NH_4)_2SO_4$, NH_4Cl, NH_4NO_3) were also compared and it was found that they have the same effect. The effect of the ammonium ion is comparable to the adipic acid as a typical additive in FGD applications.

Notation

[i]	activity of species *i*, mol L^{-1}
c_i	concentration of species *i*, mol L^{-1}
CT	total concentration of carbonate species in the solution (mass balance)
F	dimensionless quotient of undissolved limestone to initial mass
K	equilibrium constant of chemical reaction
k_{dis}	linear dissolution rate, µm s^{-1}
K_H	equilibrium constant according to Henry's law
L/G	liquid flow rate to gas flow rate volume ratio, L m^{-3}
m	mass, g
pH	$= - \log [H_3O^+]$
p_i	concentration of *i* in gas phase
$S4T$	total concentration of sulphite species in the solution (mass balance)
$S6T$	total concentration of sulphate species in the solution (mass balance)
z_i	charge of ion *I*

Greek letters

Σ	sum operator
Δ	difference

Subscripts

0	under initial conditions
$CaCO_3$	limestone
$CaSO_4$	gypsum ($CaSO_4.2H_2O$)

H_2CO_3	hydrated CO_2 in water
H_2SO_3	sulphurous acid
H_2SO_4	sulphuric acid
NH_3	ammonium
$NH_4CO_3^-$	non-dissociated ammonium carbonate anion
NH_4HCO_3	ammonium hydrogen carbonate
sp	solubility product
t	time
Superscripts	
1, 2	first and second step of chemical reaction, respectively

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Povzetek

Eksperimentalno smo izmerili in modelirali vpliv dodatka amonijevega sulfata v raztopini v mokrem kalcitem postopku za razžvepljevanje dimnih plinov termocentral. Opazili smo, da se je puferska kapaciteta povečala do 500 %. Podani so eksperimentalni podatki o hitrosti raztapljanja kalcita v pH statirani napravi v odvisnosti od različnih pomembnih parametrov (koncentracije amonijevih in kloridnih ionov, pH vrednost, temperatura). Rezultati so podani kot linearna hitrost raztapljanja kalcita (μm s^{-1}), ki je neodvisna od velikosti delcev. Ugotovili smo, da je vpliv amonijevega iona primerljiv z vplivom adipinske kisline, ki je znan dodatek v mokrih razžvepljevalnih napravah. Oba dodatka povečata pufersko kapaciteto raztopine in hitrost raztapljanja kalcita.