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SORPTION OF SULPHUR DIOXIDE IN CALCIUM CHLORIDE AND NITRATE CHLORIDE LIQUIDS

Flue gas desulphurization via application of suspensions has one inherent disadvantage: fixation of sulphur dioxide is very poor. This should be attributed to the low content of calcium ions which results from the solubility of the sorbing species. The solubility of sparringly soluble salts (CaO, $CaCO_3$) may be increased by decreasing the pH of the solution; yet, there is a serious limitation in this method: the corrosivity of the scrubber.

The objective of this paper was to assess the sorbing capacity of two soluble calcium salts, calcium chloride and calcium nitrate, as a function of calcium ion concentration in the range of 20 to 82 kg/m^3.

It has been found that sorbing capacity increases with the increasing calcium ion concentration until the calcium concentration in the calcium chloride solution reaches the level of 60 kg/m^3 which is equivalent to the chloride ion content of ~110 kg/m^3. Addition of calcium hydroxide to the solutions brings about an increase in the sorbing capacity up to 1.6 kg/m^3 and 2.2 kg/m^3 for calcium chloride and calcium nitrate, respectively, as a result of the increased sorbend alkalinity. The sorption capacity of the solutions is considerably enhanced by supplementing them by acetate ions (2.8 to 13.9 kg/m^3). Increase in the sorption capacity of calcium nitrate solutions enriched with calcium acetate was approximately 30% as high as that of the chloride solutions supplemented in the same way.

1. INTRODUCTION

One of the developmental trends in the technology of flue gas desulphurization (FGD) consists in simplifying the absorption of sulphur dioxide and in utilizing the by- or end-products [1]–[3]. In this decade preference has been given to FGD methods which make use of calcium compounds to fix the sulphur dioxide removed from the flue gas stream. Of the calcium involved, i.e., limestone, was found to be the most economic, so it has received wide application as a SO_2 sorbing agent. The sorption rate of SO_2 in aqueous suspension of limestone depends primarily on the concentration of calcium ions in the sorbing solution. It is a well-established

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fact that calcium carbonate displays a low water-solubility. That is why the pH of the sorbing suspension falls between 5 and 6, thus creating serious operation problems due to corrosion. In the past decade consideration has been given to the utility of soluble calcium salts (calcium chloride, calcium nitrate or calcium formicate) when applied in a combination with the lime or limestone suspension [2]. Each of the soluble calcium salts brings about a considerable increase of calcium ion content in the solution, and calcium formicate has the inherent advantage of maintaining a constant pH due to the buffering properties. In this way, sulphite ions produced as a result of sorption are quickly removed, thus increasing the FGD performance.

Carboxylic acids were also found to enhance FGD [4]–[6] when added in small amounts to sulphur dioxide sorbing solution. Addition of carboxylic acid to the limestone or lime suspensions increases their solubility, improves the degree utilization, and decreases the amount of wastes produced.

Absorption of sulphur dioxide in the presence of carboxylic acid involves the following processes:

1. Dissolution in water, $SO_2 + H_2O \rightleftarrows H_2SO_3$.
2. Dissociation, $H_2SO_3 \rightleftarrows H^+ + HSO_3^-$.
3. pH buffering, $RCOO^- + H^+ \rightleftarrows RCOOH$.

Addition of carboxylic acid accounts for the origin of a buffering mixture which fixes the H^+ ions produced in the course of the dissociation reaction. This leads to the shift of the reaction equilibrium to the right-hand side, thus increasing the yield of the dissolution reaction.

The FGD enhancement by carboxylic acids has a disadvantage which consists in the fact that the carboxyl ion is degraded when sulphites contained in the effluent from the sorption process are converted into sulphates. UK Patent [7] shows that the acid losses produced via this route may be limited by the addition of chloride ions to the SO_2-sorbing agent. The influence of chlorides on the performance of the FGD is interpreted in a different manner. Some of the investigators [8], [9] are of the opinion that the limit Cl^- concentration, above which the presence of chlorides has a harmful effect on the course of the sorption process, varies from 20 to 30 kg/m^3. Others [10], [11] have found that the presence of carboxylic acid diminishes the disadvantageous influence of the Cl^- ions. Thus, the absorption of sulphur dioxide may also be efficient at increased concentrations of chlorides.

The objective of this study was to determine the sorption capacity of sulphur dioxide in calcium chloride and calcium nitrate solutions as well as in the solutions modified by calcium hydroxide or calcium acetate.

2. EXPERIMENTAL

2.1. PLANNING OF THE EXPERIMENT

The sorbing capacity of soluble calcium salts was investigated in three steps: 1) the sorbing capacities of calcium chloride, calcium nitrate, and calcium hydroxide solutions were measured as functions of their concentrations; 2) the sorbing capacities of calcium chloride and calcium nitrate of determined concentrations were measured as functions of the calcium hydroxide additive, and 3) the sorbing capacities of calcium chloride and calcium nitrate solutions were measured as functions of the calcium acetate additive or as functions of a combined addition of acetic acid (equivalent to the acetate ion) and calcium hydroxide.

2.2. MEASURING PROCEDURES

Gaseous sulphur dioxide produced during the hydrosulphite degradation [12] was passed at room temperature through the solution of a 100 cm^3 volume and a determined composition. There was simultaneous recording of pH. After the pH of the sorbent had reached the value of 3.7 to 3.9, the sorption process was regarded as being completed. The sorbing capacity was defined as the ratio of the sulphur dioxide quantity absorbed to the volume of the solution (in kg/m^3). The quantity of sulphur dioxide absorbed was established analytically by determining the oxygen compounds of sulphur which originated in the solution and in the sediment.

3. RESULTS AND DISCUSSION

The results are given in tabs. 1–4 and figs. 1–7.

Sorption of sulphur dioxide in the calcium liquids under study proceeded without precipitation of sediments for the whole range of Ca^{2+} concentration (from 20 to 82 kg/m^3), and pH reached the value required within a very short time. Calcium chloride and calcium nitrate displayed similar sorbing capacities (0.1 to 0.3 kg/m^3) which increased with the increasing

Table 1

Sorbing capacities of calcium solutions as a function of calcium ion concentration

No. of sample	Type of solution	Concentration (kg/m^3) Salt	Ca^{2+}	Cl$^-$ or NO$_3^-$	pH before sorption	pH after sorption	Sorbing capacity (kg/m^3)
1'	CaCl$_2$	56.9	20.5	36.4*	7.24	3.7	0.157
2'		114.0	41.1	72.8*	7.13	3.8	0.228
3'		171.2	61.7	109.5*	7.07	3.8	0.275
4'		227.8	82.1	145.7*	6.93	3.75	0.253
1"	Ca(NO$_3$)$_2$	83.2	20.3	62.9**	6.25	3.75	0.101
2"		186.1	45.4	140.7**	6.15	3.8	0.169
3"		253.4	61.8	191.6**	6.05	3.8	0.182
4"		336.6	82.1	254.5**	5.95	3.8	0.218
1	Ca(OH)$_2$	1.340	0.724	–	12.10	2.2	1.99
2		1.460	0.789	–	12.45	3.8	1.32
3		0.365	0.197	–	11.80	3.8	0.42

* Cl$^-$ ions.

** NO$_3^-$ ions.

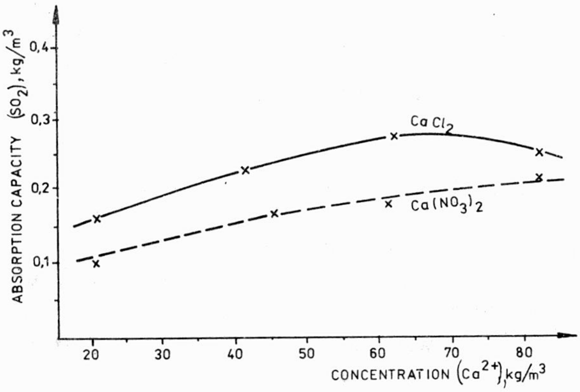

Fig. 1. Sorption capacity of calcium chloride or calcium nitrate solutions as a function of calcium ion concentration

concentration of calcium ions. The sorbing capacity of the calcium chloride solution reached its maximum value at the calcium ion concentration of 60 kg/m^3 (109.5 kg Cl$^-$/m^3) and then decreased. No such a maximum was found to occur for calcium nitrate in the investigated range of calcium ion concentration. The decreased sorbing capacity of the calcium chloride solution is likely to be due to the increase in the ionic strength of the solution with the increasing salt concentration, as well as to the decrease in ionic activity. The influence of nitrate ion concentration is slightly weaker.

To investigate the effect of the increasing calcium hydroxide concentration on the sorbing capacity of the investigated calcium-based liquids, we made use of the samples which displayed low calcium ion concentrations (~20 kg/m^3). In the course of the sorption process, calcium

Table 2

Sorbing capacities of calcium chloride and calcium nitrate solutions at constant calcium ion concentration (~20 kg/m^3) as a function of mass of calcium hydroxide additive

No. of sample	Type of solution	$Ca(OH)_2$ additive (kg/m^3)	pH before sorption	pH after sorption	SO_2 absorbed In solution (kg/m^3)	SO_2 absorbed In slurry (kg/m^3)	Sorbing capacity (kg/m^3)
1′	$CaCl_2$	0.364	10.95	3.96	0.643	–	0.643
2′	56.9 kg/m^3	0.657	11.65	3.70	0.951	–	0.951
3′		0.949	11.85	3.75	1.430	–	1.430
4′		1.204	12.05	3.75	1.522	–	1.522
5′		1.460	12.35	3.75	1.441	–	1.441
1″	$Ca(NO_3)_2$	0.364	8.90	3.85	0.725	–	0.725
2″	83.2 kg/m^3	0.657	9.40	3.75	0.492	0.411	0.903
3″		0.949	9.85	3.70	0.662	0.733	1.395
4″		1.204	10.26	3.75	0.735	0.874	1.609
5″		1.460	11.75	3.75	0.895	1.310	2.205

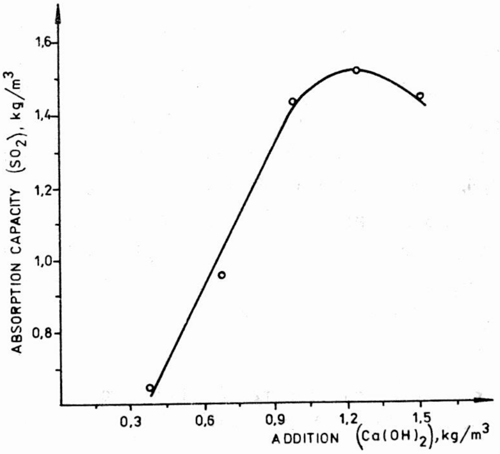

Fig. 2. Sorption capacity of calcium chloride solution as a function of calcium hydroxide additive

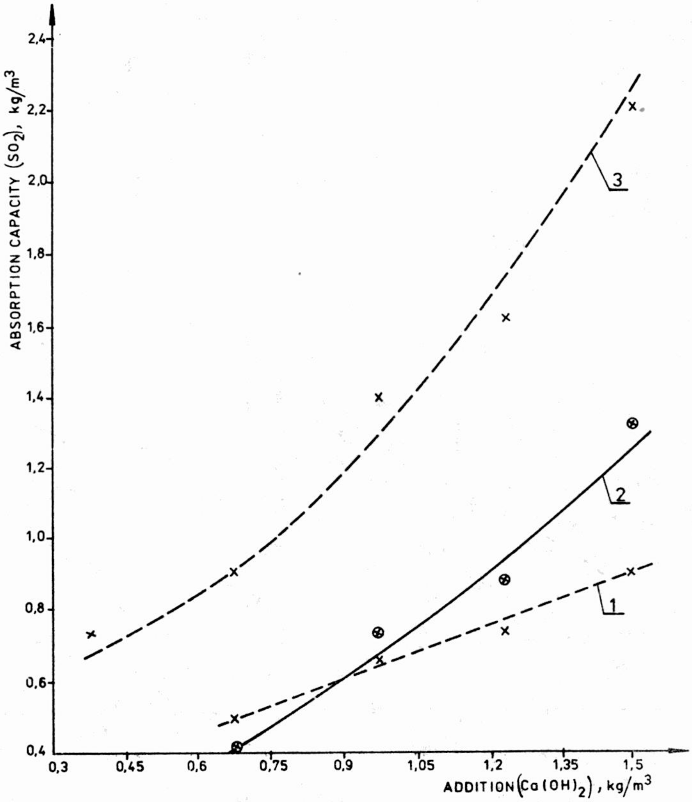

Fig. 3. Sorption capacity of calcium nitrate solution as a function of calcium hydroxide additive
1 – sulphur dioxide in the form of sulphate ions (in the solution), *2* – sulphur dioxide in the form of sulphite ions (in the sediment), *3* – total sulphur dioxide content

sulphite sediments persisted in the calcium nitrate solution, irrespective of the calcium hydroxide quantity added (from 0.657 kg/m^3 up to saturation). The sediments in calcium chloride solutions dissolved at the final stage of the sorption process. This behaviour is to be attributed to the varying initial alkalinity of the sorbing solutions. The decreased pH of the nitrate solutions at high concentration of calcium ions accounts for the shift of the pH limit at which appropriate ion equilibria occur and contributes to the occurrence of sediments at pH ranging between 3.75 and 3.9. There is also a difference in the character of the nitrate ions and the chloride ions, especially in their ability to form complexes. In both types of solutions, sulphur dioxide content after sorption increased with the increasing amount of calcium hydroxide. Saturated calcium chloride solution showed a slight decrease in sorbing capacity.

Table 3

Sorbing capacities of calcium chloride and calcium nitrate solutions at constant calcium ion concentration (~20 kg/m^3) as a function of mass of calcium acetate additive

No. of sample	Type of solution	Acetate additive (kg/m^3)	pH before sorption	pH after sorption	SO_2 absorbed: In solution (kg/m^3)	SO_2 absorbed: In slurry (kg/m^3)	Sorbing capacity (kg/m^3)
1′	$CaCl_2$	3.72	7.87	3.8	1.718	–	1.72
2′	56.9 kg/m^3	7.43	7.95	3.8	2.168	1.215	3.38
3′		11.15	7.95	3.8	1.882	2.467	4.35
4′		14.87	7.97	3.8	2.058	3.816	5.87
5′		18.58	7.85	3.8	1.373	4.716	6.09
1″	$Ca(NO_3)_2$	3.72	6.75	3.8	2.239	–	2.24
2″	83.2 kg/m^3	7.43	6.90	3.8	2.253	1.818	4.07
3″		11.15	7.02	3.8	1.870	2.506	4.38
4″		14.87	7.10	3.8	2.650	3.911	6.56
5″		18.58	7.20	3.85	4.856	4.239	9.09

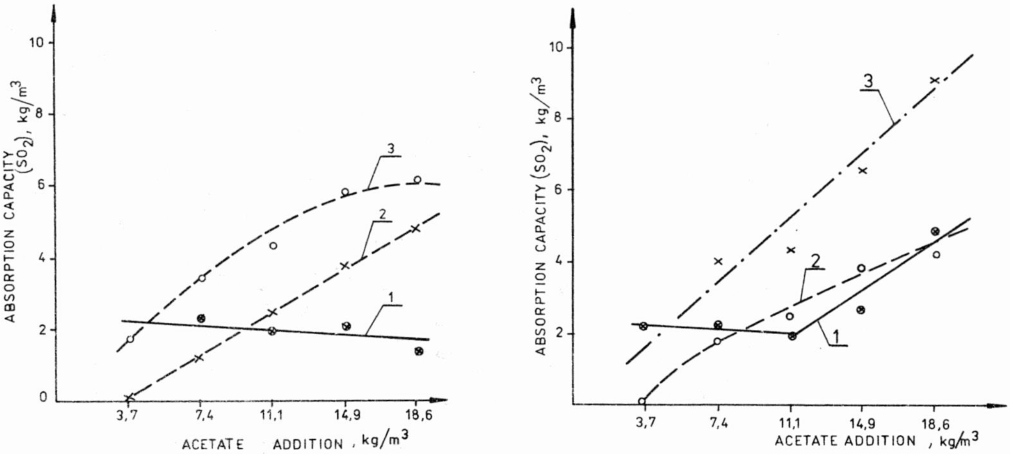

Fig. 4. Sorption capacity versus calcium acetate content in calcium chloride solution (4a) and calcium nitrate solution (4b) at calcium ion concentration of ~20 kg/m^3

1 – sulphur dioxide in the form of sulphate ions (in the solution), *2* – sulphate dioxide in the form of sulphite ions (in the sediment), *3* – total sulphur dioxide content

Absorption of sulphur dioxide in calcium chloride and calcium nitrate solutions of a constant calcium ion concentration (~20 kg/m^3) supplemented by various calcium acetate doses (3.7 to 18.6 kg/m^3) began to run with precipitation of sediments when the calcium acetate addition amounted to 7.4 kg/m^3. This behaviour should be attributed to the introduction of additional calcium ions (which influenced the ion equilibrium in the solutions) and to the increase in alkalinity caused by the hydrolysis of acetate. As the quantity of the acetate additive

Table 4

Sorbing capacities of calcium chloride and calcium nitrate solutions acidified with acetic acid and alkalized with calcium hydroxide at constant concentration (~20 kg/m^3) of calcium ions

No. of sample	Type of solution	CH_3COOH additive (kg/m^3)	pH following addition of		pH after sorption	SO_2 absorbed		Sorbing capacity (kg/m^3)
			CH_3COOH	$Ca(OH)_2$		In solution (kg/m^3)	In slurry (kg/m^3)	
1′	$CaCl_2$	2.82	3.2	11.65	3.8	1.51	2.04	3.55
2′	56.9 kg/m^3	5.64	2.9	11.77	3.8	2.19	3.17	5.36
3′		8.47	2.77	11.62	3.8	2.61	4.17	6.78
4′		11.29	2.67	11.67	3.8	2.22	5.75	7.97
5′		14.11	2.62	11.80	3.8	2.57	6.46	9.03
1″	$Ca(NO_3)_2$	2.82	2.85	11.75	3.82	1.66	2.80	4.46
2″	83.2 kg/m^3	5.64	2.70	11.80	3.80	2.09	3.55	5.66
3″		8.47	2.62	11.65	3.70	2.66	4.45	7.61
4″		11.29	2.55	11.82	3.80	2.86	5.80	9.34
5″		14.11	2.51	11.75	3.80	3.15	8.87	12.02

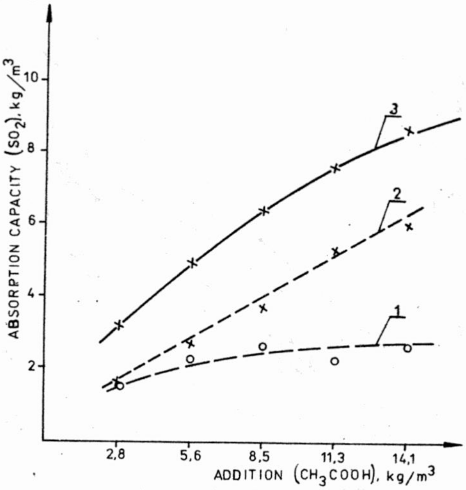

Fig. 5. Sorption capacity versus acetate in calcium chloride solution (at calcium ion concentration of ~20 kg/m^3) enriched with calcium oxide

1 – sulphur dioxide in the form of sulphate ions (in the solution), *2* – sulphur dioxide in the form of sulphite ions (in the sediment), *3* – total sulphur dioxide content increased, so did the quantity of the precipitated sediment, whereas the amount of sulphur dioxide (which occurred in the form of HSO_3^-, SO_3^{2-}, and HSO_4^-) remainded approximately on the same level. The presence and concentration of ions in the solutions depend primarily on pH (which is stabilized by acetate and acetic acid) and, also, on the activity of associated ions (their type and concentration). The sorbing capacities of the calcium chloride and calcium nitrate solutions vary from 1.72 to 6.09 kg/m³ and from 2.2 to 9.1 kg/m³, respectively.

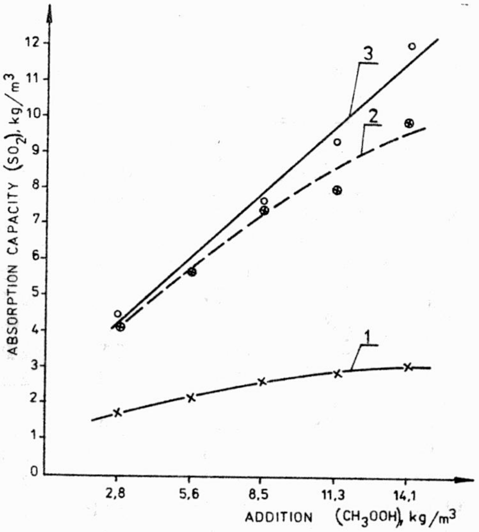

Fig. 6. Sorption capacity versus acetate content in calcium nitrate solution (at calcium ion concentration of ~20 kg/m³) enriched with calcium hydroxide

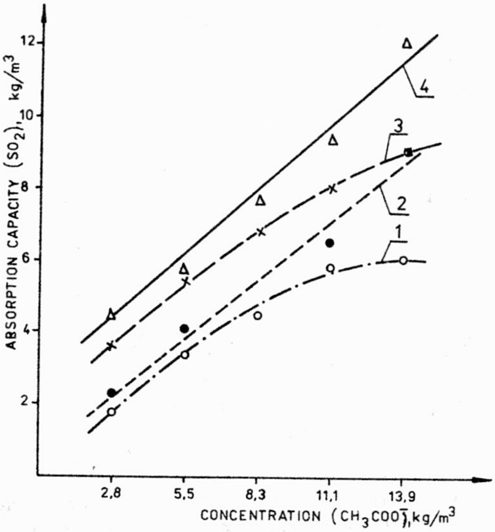

Fig. 7. Sorption capacity versus acetate ion concentration in calcium chloride solution (curve *1* and curve *3*) and calcium nitrate solution (curve *2* and curve *4*) enriched with acetic acid (curve *3* and curve *4*) or calcium acetate (curve *1* and curve *2*)

There were measured the sorption capacities of both mentioned liquids in which acetate was replaced by acetic acid and calcium hydroxide in the amount guaranteeing saturation of the solutions with hydroxide. There was a general increase in sorbing capacity when calcium hydroxide occurred in excess. Thus, at the highest CH_3COO^- ion content in the sorbent, sorbing capacity was found to increase from 6.09 to 9.03 kg/m^3 and from 9.09 to 12.02 kg/m^3 for calcium chloride solution and nitrate chloride solution, respectively. This increase is due to the increasing alkalinity which accounts for the rise in the precipitation of calcium sulphite sediments.

4. CONCLUSIONS

1. The sorbing capacity of pure calcium chloride and calcium nitrate solutions is poor (0.1 to 0.3 kg/m^3) and increases slightly with the increasing content of calcium ions.

2. At a constant concentration of calcium ions in the solution, its sorbing capacity depends on the mass of the calcium hydroxide additive and increases with the increasing calcium hydroxide content to reach a maximum of 1.6 kg/m^3 and 2.2 kg/m^3 for calcium chloride and calcium nitrate, respectively. In every instance, the sorbing capacity of the solution enriched with calcium hydroxide is higher than that of the saturated calcium hydroxide solution (tab. 1, sample 2).

3. The sorbing capacity of calcium chloride and calcium nitrate solutions at a constant concentration depends on the mass of the calcium acetate additive and increases with it.

4. When acetic acid is added to the sorbing solutions instead of acetate (the quantity of acetate ions being constant), the decreased pH value must be adjusted by the addition of calcium hydroxide.

5. Calcium nitrate solution enriched with the calcium acetate displays an increased sorbing capacity as compared to that of the calcium chloride solution treated with the same additive.

6. The end product of the FGD process, i.e., gypsum, contaminated with calcium nitrate is readier for reuse than that contaminated with calcium chloride.

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BADANIE SORPCJI DWUTLENKU SIARKI W ROZTWORACH CHLORKU WAPNIOWEGO I AZOTANU WAPNIOWEGO

Zawiesinowe metody odsiarczania gazów odlotowych charakteryzują się niską wydajnością wiązania dwutlenku siarki. Jest to spowodowane niską zawartością jonów wapniowych w roztworze. Rozpuszczalność soli typu CaO i $CaCO_3$ wzrasta z obniżeniem pH; małe wartości pH są jednak ograniczone korozyjnością aparatury sorpcyjnej.

Oceniono zdolności sorpcyjne rozpuszczalnych soli wapniowych, chlorku i azotanu wapniowego, w zależności od stężenia Ca^{2+} (w zakresie 20–82 kg/m^3). Stwierdzono, że pojemność sorpcyjna roztworu soli wzrasta ze zwiększeniem stężenia Ca^{2+} aż do wartości 60 kg/m^3, co odpowiada zawartości ~110 kg/m^3 jonów Cl^-.

Dodatek $Ca(OH)_2$ do roztworów, przy ich stałym stężeniu, zwiększał pojemność sorpcyjną soli $CaCl_2$ i $Ca(NO_3)_2$ do 1,6 i 2,2 kg/m^3 z powodu wzrostu alkaliczności sorbentów. Dużo większy wzrost pojemności sorpcyjnej uzyskano dzięki wprowadzeniu do badanych roztworów jonów octanowych (2,8–13,9 kg/m^3). Wzrost pojemności sorpcyjnej roztworów azotanowych w kompozycji z octanem wapniowym był o około 30% większy od takich samych roztworów chlorkowych, co wskazywałoby na mniej korzystny wpływ jonów azotanowych na proces sorpcji SO_2.

ИССЛЕДОВАНИЕ СОРБЦИИ ДВУОКИСИ СЕРЫ В РАСТВОРАХ ХЛОРИДА КАЛЬЦИЯ И НИТРАТА КАЛЬЦИЯ

Взвешенные методы обессерения отходящих газов характеризуются низкой эффективностью связывания двуокиси серы. Это вызвано малым содержанием ионов кальция в растворе. Растворимость солей типа CaO, $CaCO_3$ растет с понижением pH; низкие значения pH ограничены однако коррозионностью сорбционной аппаратуры. Оценены сорбционные способности растворимых кальциевых солей хлорида и нитрата кальция в зависимости от концентрации Ca^{2+} (в пределах 20–82 кг/м^3). Было установлено, что сорбционная емкость раствора соли растет вместе с повышением концентрации Ca^{2+} вплоть до значения 60 кг/м^3, что отвечает содержанию ~110 кг/м^3 ионов Cl^-.

Добавление $Ca(OH)_2$ к растворам, при их постоянной концентрации, повышало сорбционную емкость до 1,6 и 2,2 кг/м^3 для $CaCl_2$ и $Ca(NO_3)_2$ из-за повышения щелочности сорбентов. Намного выше рост сорбционной емкости получен благодаря введению к исследуемым растворам ацетат-ионов (2,8–13,9 кг/м^3). Повышение сорбционной емкости нитратных растворов в композиции с ацетатом кальция было на ~30% выше таких же хлоридных растворов, что указывало бы на менее полезное влияние хлор-ионов чем ацетат-ионов на процесс сорбции SO_2.