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OXIDATION OF CALCIUM SULPHITE IN SUSPENSION

Oxidation of sulphites is an effective step in flue gas desulphurization by lime treatment. The efficiency of the oxidation of sulphites to calcium sulphate accounts for the quality and, consequently, for the utilization of the end-product, viz. gypsum. Thus, the main objective of this study was to determine and factor contributing to the efficiency of the oxidation reaction.

Experiments were run with 1 to 3 wt% concentration suspensions, which were oxidized at 293 K and an air flow rate ranging within $5.55 \cdot 10^{-6} - 1.9 \cdot 10^{-5} \text{ m}^3/\text{s}$. Analysis of results showed that two factors, i.e., the pH of the suspension and the presence of a catalyst, primarily affected the degree of oxidation. The contribution of the cobalt catalyst was investigated as a function of time and pH. Addition of 0.05% catalyst (with regard to CaSO_3) to 1 wt% suspension at pH = 5.5 yields an approximately 84% conversion of sulphites to calcium sulphate after 60 min of oxidation. The increase of catalyst concentration reduces the duration of the oxidation reaction.

1. INTRODUCTION

Flue gas desulphurization (FGD) by wet processes gives solutions, slurries and sediments as waste products. Their composition depends on the sorbent used and on the course of the process. The FGD process can be conducted so as to obtain either calcium sulphite or calcium sulphate as one of the final compounds. When the solutions obtained due to sorption contain sulphites, the regeneration process is far more effective than that for the solutions containing sulphates. But there appear serious troubles with the separation, storage or utilization of the product. As a result of some disadvantageous properties (e.g., thixotropy) of $\text{CaSO}_3 \cdot 1/2 \text{ H}_2\text{O}$, sulphite slurry retains large amounts of water, which makes its filtration and storage a difficult task [1].

Oxidation of sulphites in solution or suspension with gypsum as the end-product can make FGD a no-waste technology. The oxidation process is conducted either in the sorption system, or out of it, depending on the system or the technology applied. It is the technological system that implies the mechanism of oxidation.

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When carried out inside the sorption system, oxidation of calcium sulphite to gypsum involves, for example, the Saarberg-Hoelter [2] or the Chiyoda Thoroughbred 121 [3] method. When conducted outside the system, the process requires application of the limestone method with forced oxidation [4].

Oxidation of sulphites to sulphates in suspension was the objective of many experimental studies [5], [6]. However, the conclusions on the mechanism governing the process or on the contributing factors are contradictory in many instances. Taking the above into account, we initiated our study of the oxidation of calcium sulphite in suspension. The objective was to determine the factors affecting the efficiency of oxidation of calcium sulphites to gypsum.

It has been assumed that the contributing factors can be itemized as follows:

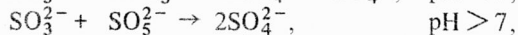
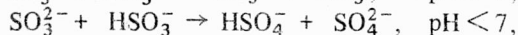
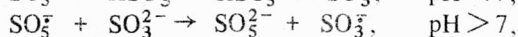
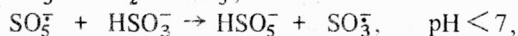
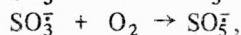
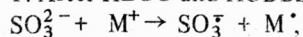
1. Concentration of the suspension (C_s).
2. Sulphite content in the suspension ($(CaSO_3)_t$).
3. Flow rate of air (Q).
4. pH of the suspension.
5. Concentration and type of the catalyst (C_c).
6. Time of oxidation (t).

2. THEORETICAL BACKGROUND

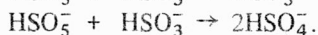
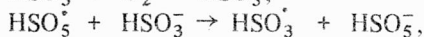
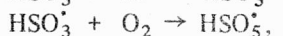
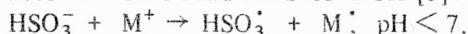
2.1. MECHANISM OF OXIDATION

The oxidation of sulphite ion (SO_3^{2-}) to sulphate ion (SO_4^{2-}) is a classical chain reaction. Although the reaction has been well described in the literature, the oxidation mechanism is still far from being well understood. The course of the process depends primarily on the pH of the solution, which is influenced by the presence of radicals (HSO_3^\cdot or HSO_5^\cdot and SO_3^\cdot or SO_5^\cdot), the intermediate products of the process. Below there are presented some examples which illustrate the course of the oxidation and its mechanisms (after [7], [8] and [9]).

1. After HEGG and HOBBS [7].

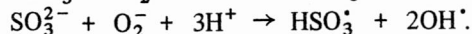
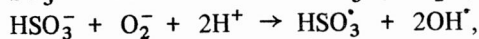
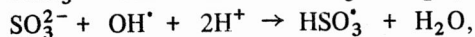
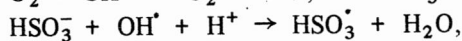
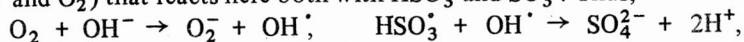


2. After GOMÓŁKA and SZAYNOK [8]:



M^+ denotes the cation of transition metal initiating the chain reaction (catalyst).

3. According to TRZEŚNIEWSKI [9]. It is particularly dissolved oxygen (in the form of OH^\cdot and O_2^-) that reacts here both with HSO_3^- and SO_3^{2-} . Thus,



As shown by these mechanisms, both HSO_3^- and SO_3^{2-} oxidize via the formation of the HSO_3^\cdot radical which can be regarded as an indication that the oxidation of the calcium sulphite suspension proceeds via several steps, the main step occurring in solution, in the presence of the HSO_3^- ion and the HSO_3^\cdot radical. Thus, oxidation in suspension is limited by the solubility of calcium sulphite in solution [10].

The solubility of calcium sulphite in aqueous solutions is not only a function of temperature and pH, but also of the concentration of the solution components [11]. If so, we should regard them as the major factors responsible for the oxidation rate.

3. EXPERIMENTAL

3.1. APPARATUS AND MEASURING METHODS

The oxidation of calcium sulphite in suspension was investigated in a glass reactor with bottom supply of air through a sinter covering the entire section (12.6 cm^2) of the apparatus. Air flow rate was measured by means of a rotameter. $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ samples (each of 50 cm^3 volume and appropriate concentration) were prepared under laboratory conditions. CaSO_3 content in the sediment varied from 68 to 70 wt%. Oxidation was run at 293 K. CoCl_2 in solution was used as catalyst in amounts corresponding to 0.01–0.1 wt% of Co^{2+} in respect of CaSO_3 .

In the course of the oxidation process 5 cm^3 samples of the suspension for analysis were collected at determined time intervals, pH variations were recorded concurrently.

3.2. ANALYTICAL PROCEDURES AND CALCULATING METHODS

Samples of calcium sulphite suspensions were collected in the course of the oxidation process and were analyzed iodometrically to determine the CaSO_3 content.

The degree of oxidation of sulphites to calcium sulphates was calculated as follows:

$$U = \frac{(\text{CaSO}_3)_i - (\text{CaSO}_3)_f}{(\text{CaSO}_3)_i} \cdot 100\%$$

where U is degree of oxidation (%), $(\text{CaSO}_3)_i$ is initial CaSO_3 content in the suspension (kg/m^3), and $(\text{CaSO}_3)_f$ is final sulphities content in the suspension (expressed as CaSO_3 in kg/m^3) after a determined of oxidation.

4. RESULTS AND DISCUSSION

The data obtained in this study are listed in tabs. 1–5 and plotted in figs. 1–4.

Table 1 gives the parameters that describe the air flow through the CaSO_3 suspension in the reactor. In fig. 1 the degree of calcium sulphite oxidation is related to the duration of the process and the rate of air flow for two concentrations (1 wt% and 3 wt%) of the suspension. As shown by these data, the increase in the air flow rate (from $5.55 \cdot 10^{-6}$ to $1.9 \cdot 10^{-5} \text{ m}^3/\text{s}$) accounts for the decrease in the degree of oxidation, irrespective of concentration and time. This is not surprising, because the increasing air flow rate reduces the time of contact between the reacting phases (tab. 1). Increased oxidation efficiencies have been obtained for suspensions of lower concentrations at the same flow rate. This increase is due to the more efficient of the solid phase particles because of their lower content in the suspension. The remaining experiments were run at an air flow rate of $8.33 \cdot 10^{-6} \text{ m}^3/\text{s}$. Flow rates below this value do not allow continual motion of particles.

Table 1
Parameters of air flow through CaSO_3 suspension in a 12.6 cm^2 section reactor

Flow rate	Linear velocity	Height of suspension column	Time of phase contact
m^3/s	m/s	m	s
$5.55 \cdot 10^{-6}$	$0.44 \cdot 10^{-2}$	$6.9 \cdot 10^{-2}$	15.7
$0.33 \cdot 10^{-6}$	$0.66 \cdot 10^{-2}$	$7.1 \cdot 10^{-2}$	10.7
$1.9 \cdot 10^{-5}$	$1.5 \cdot 10^{-2}$	$7.9 \cdot 10^{-2}$	5.3

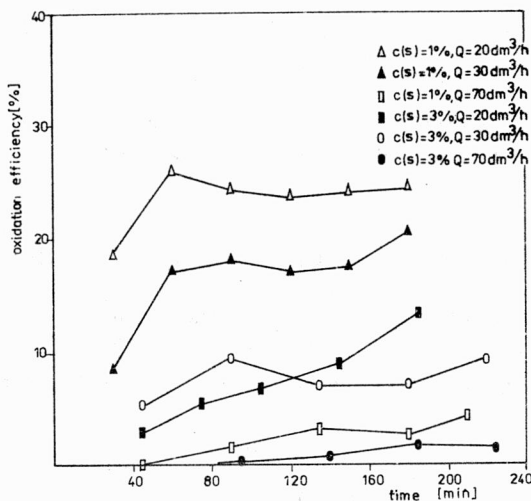


Fig. 1. Efficiency of oxidation as a function of time and air flow rate (at $\text{pH} = 7$)

Table 2

Oxidation of CaSO_3 as a function of time (t), air flow rate (Q) and suspension concentration (C_s),
 $T = 293 \text{ K}$, $(\text{CaSO}_3)_i = 75\%$, $\text{pH} = 7,0$

C_s	$Q \text{ (dm}^3/\text{h)}$											
	20				30				70			
	t	pH	$(\text{CaSO}_3)_f$	U	t	pH	$(\text{CaSO}_3)_f$	U	t	pH	$(\text{CaSO}_3)_f$	U
%	min		kg/m ³	%	min	kg/m ³	%	min		kg/m ³	%	
1	30	7.15	6.10	18.6	30	6.9	6.86	8.5	45	6.55	7.52	0
	60	7.10	5.56	25.9	60	6.3	6.21	17.2	90	6.95	7.38	1.57
	90	7.10	5.68	24.2	90	5.8	6.14	18.1	135	7.0	7.26	3.20
	120	7.10	5.77	23.7	120	—	6.22	17.1	180	7.3	7.29	2.7
	150	7.20	5.70	24.0	150	5.8	6.19	17.5	210	6.9	7.18	4.30
	180	7.15	5.68	24.3	180	—	5.96	20.4	—	—	—	—
3	45	6.9	21.86	2.84	45	6.95	21.37	5.2	45	6.2	22.4	0
	75	6.6	21.27	5.47	90	6.9	20.37	9.47	95	6.0	22.7	0.25
	105	7.0	21.0	6.7	135	6.95	20.92	7.02	140	—	22.33	0.75
	145	7.05	20.49	8.9	180	7.05	20.93	7.02	185	6.8	22.11	1.7
	185	—	19.48	13.42	220	6.95	20.37	9.47	225	6.9	22.16	1.5

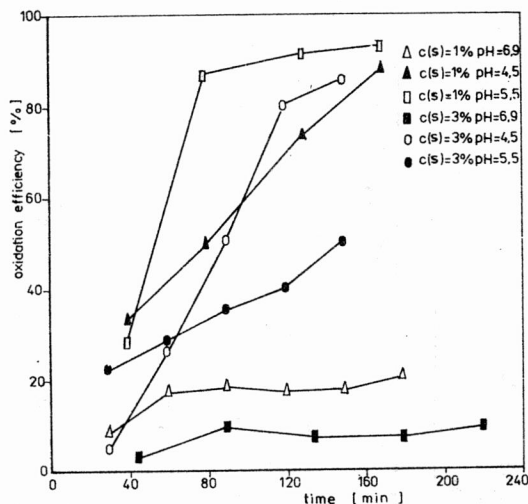


Fig. 2. Efficiency of oxidation as a function of time and pH
(at $Q = 8.33 \cdot 10^{-6} \text{ m}^3/\text{s}$)

Figure 2 presents the effect of pH (in the range from 4.5 to 7) on the degree of oxidation of suspensions the concentrations of which equal to 1 and 3 wt%. As shown by these plots, the contribution of pH is considerable. The highest oxidation efficiency, i.e., 86.5%, was achieved for the 1 wt% suspension at pH = 5.5, after a time of 80 min. The highest degree of oxidation for the 3 wt% suspension was obtained at pH = 4.5 and also after 80 min, but it amounted only to 45%.

The rate of oxidation is influenced by the dissolution of the calcium sulphite sediments, which increases when pH decreases. But it may also be the desorption of SO_2 (which initiates at pH approaching 4) that accounts for the increasing oxidation values. It should be noted, however, that in the course of the process there may occur a temporary drop of pH below 4.5. Irrespective of other contributing factors, favourable conditions for the oxidation of sulphites are created when the pH of the suspension ranges between 4.5 and 5.5. However, taking into account the possible onset of SO_2 desorption, the oxidation process should be conducted at pH = 5.5, regardless of the suspension concentration.

Another factor, which strongly affects the degree of calcium sulphite oxidation, is the presence of the catalyst (fig. 3). Addition of the Co^{2+} catalyst in amounts of 0.05 wt% of sulphite content raises the degree of oxidation from a dozen or so to several dozen per cent. The increase of the Co^{2+} content in the suspension up to 0.1% increases the efficiency of oxidation from 75 to approximately 100% in the time of 90 min. In other words the rise in Co^{2+} content reduces the time required for achieving complete oxidation of sulphites.

Table 4

Oxidation of CaSO_3 as a function of time (t), suspension concentration (C_s) and cobalt catalyst addition (C_c),
 $T \approx 293 \text{ K}$, $\text{pH} = 7.0$, $Q = 30 \text{ dm}^3/\text{h}$ ($8.33 \cdot 10^{-6} \text{ m}^3/\text{s}$), $(\text{CaSO}_3)_i = 75\%$

C_s	Co^{2+} catalyst concentration (%)											
	0.01				0.05				0.1			
	t	pH	$(\text{CaSO}_3)_f$	U	t	pH	$(\text{CaSO}_3)_f$	U	t	pH	$(\text{CaSO}_3)_f$	U
%	min		kg/m^3	%	min	kg/m^3	%	min		kg/m^3	%	
1	30	6.85	5.92	21.0	40	7.1	5.015	33.1	30	7.2	2.93	60.9
	60	6.8	5.95	20.7	90	7.2	1.81	75.0	60	7.1	0.16	97.9
	90	6.95	5.99	20.2					90	7.15	0.00	100.0
	120	7.0	6.00	20.0	130	7.15	0.04	99.5				
	150	7.2	5.96	20.6	170	6.8	0.00	100.0	120	—		
	180	6.7	5.89	21.5								
3	40	7.2	18.84	15.27	30	6.95	19.98	11.2	30	6.8	15.57	30.8
	90	7.1	19.33	14.10	60	6.9	19.09	15.1	60	6.1	14.44	35.8
	130	7.15	20.0	11.0	90	7.15	18.46	17.9	90	6.0	12.60	44.0
	170	7.25	18.84	16.27	120	7.10	12.45	44.7	120	6.05	10.23	54.5
					150	7.15	2.46	89.0	150	6.2	3.20	85.8
					180	7.25	0.16	99.3	180	6.0	1.20	94.7

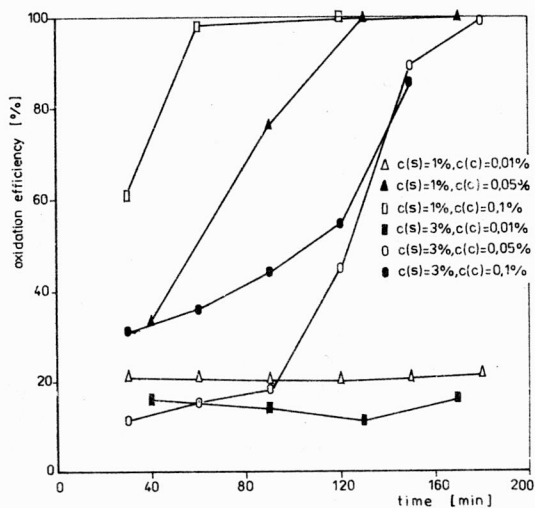


Fig. 3. Efficiency of oxidation as a function of cobalt catalyst addition (at pH = 7)

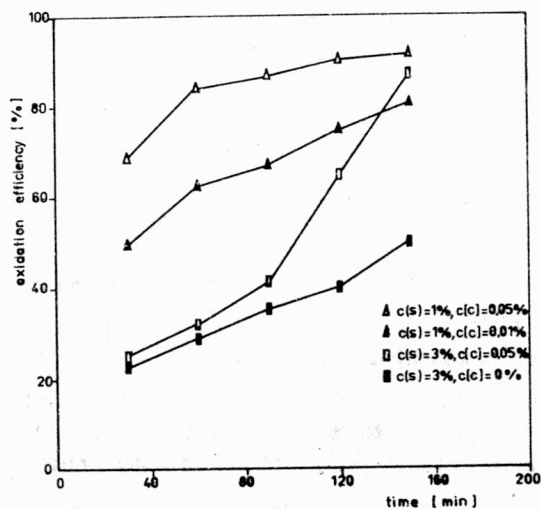


Fig. 4. Efficiency of oxidation as a function of cobalt catalyst addition (at pH = 5.5)

Figure 4 gives the relationship between oxidation efficiency and Co^{2+} addition (at pH = 5.5). From these curves it is seen that, as the catalyst dose increases, so does the degree of oxidation. Thus, a Co^{2+} dose of 0.05 wt% yields an oxidation efficiency of about 84% after 60 min of contact. Further increase in the degree of oxidation proceeds slowly up to 91% (maximum value).

The increase of oxidation with the increasing catalyst dose is more pronounced in the suspension of lower concentration.

Table 5

Oxidation of CaSO_3 as a function of time (t), suspension concentration (C_s) and cobalt catalyst addition (C_c), pH = 5.5, $T = 293 \text{ K}$, $(\text{CaSO}_3)_i = 75\%$

C_s	Co ²⁺ catalyst addition (%)							
	0.01				0.05			
	t	pH	$(\text{CaSO}_3)_f$	U	t	pH	$(\text{CaSO}_3)_f$	U
%	min		kg/m ³	%	min	kg/m ³	%	
1	30	5.5	3.82	49.1	30	5.5	2.38	68.3
	60		2.85	62.0	60		1.21	83.9
	90		2.50	66.7	90		1.01	86.5
	120		1.91	74.5	120		0.74	90.1
	150	4.5	1.48	80.3	150	4.27	0.66	91.2
3	30	5.5	16.90	24.9				
	60		15.26	32.2				
	90		13.16	41.5				
	120		7.92	64.8				
	150	5.1	2.93	87.0				

5. CONCLUSIONS

1. Our study enabled determination of the parameters contributing to the oxidation efficiency of calcium sulphite.

2. Of the various contributing factors two are particularly effective — pH of the suspension and concentration of the catalyst.

3. Catalyst activity increases with decreasing pH.

4. Appropriate choice of pH (5.5), Co²⁺ catalyst concentration (0.1%) and air flow rate ($8.33 \cdot 10^{-6} \text{ m}^3/\text{s}$) makes it possible to reduce the oxidation time of calcium sulphite and to achieve a sufficient oxidation of the suspension at a given concentration.

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UTLENIANIE SIARCZYNU WAPNIOWEGO W ZAWIESINIE

Utlenianie siarczynów z zastosowaniem związków wapnia jest jednym z ważniejszych etapów procesu odsiarczania gazów odlotowych. Stopień utlenienia siarczynów do siarczanu wapniowego decyduje o jakości gipsu, a więc i o możliwościach jego wykorzystania. Dlatego też podjęto badania nad utlenianiem siarczynu wapniowego. Celem ich było określenie czynników wpływających na stopień utlenienia. Na podstawie wyników badań nad utlenianiem zawiesiny o stężeniu 1–3% wagowych w temperaturze 293 K i przy natężeniu przepływu powietrza $5,55 \cdot 10^{-6}$ – $1,9 \cdot 10^{-5}$ m³/s ustalono, że najważniejszymi czynnikami są odczyn i obecność katalizatora. Przebadano wpływ katalizatora kobaltowego na stopień utleniania w zależności od czasu utleniania i pH zawiesiny. Dodatek 0,05% katalizatora w 1% zawiesinie CaSO₃, przy pH = 5,5, pozwala osiągnąć po 1 h utleniania prawie 84% stopień przemiany siarczynów. Wzrost stężenia katalizatorów skraca czas utleniania.

ОКИСЛЕНИЕ СУЛЬФИТА КАЛЬЦИЯ В СУСПЕНЗИИ

Окисление сульфитов является одним из важнейших этапов процесса обессерения отходящих газов с применением соединений кальция. Степень окисления сульфитов до сульфата кальция решает о качестве, а затем о возможностях сульфата кальция. Целью исследований было определение факторов, влияющих на степень окисления. На основе результатов исследований окисления суспензии концентрации 1–3% веса в температуре 293 К и при напряжении течения воздуха $5,55 \cdot 10^{-6}$ – $1,9 \cdot 10^{-5}$ м³/с установили, что к самым важным факторам относятся реакция и наличие кatalизатора. Исследовано влияние кобальтового кatalизатора на степень окисления в зависимости от времени окисления и pH в суспензии. Добавление 0,05% кatalизатора по отношению к CaSO₃ в 1% суспензии при pH = 5,5 позволяет достиг после 1 ч окисления степень превращения сульфитов ~84%. Повышение концентрации кatalизатора сокращает время окисления.