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OXIDATION OF CALCIUM SULPHITE COMING FROM FLUE GAS DESULPHURIZATION IN THE PRESENCE OF AN IRON CATALYST

Oxidation of sulphites is a major step in flue gas desulphurization. The efficiency with which calcium sulphites (obtained during sorption of SO_2 involving lime treatment) are oxidized accounts for the quality and, consequently, for the utilization of the end-product, i.e., gypsum. The efficiency of the oxidation process is influenced by a number of different factors. Of these, the pH of the solution and the presence of a catalyst in the reaction medium deserve special attention. Of the transition metals that are found in the medium of sulphites oxidation, iron is the most common. Thus, the main objective of this study was to investigate the effect of Fe^{3+} on the efficiency of calcium sulphite oxidation. Experiments were run with 1–5 wt.% $CaSO_3$ suspensions, which were oxidized at 293 K and an air flow rate of $8.33 \cdot 10^{-6}$ m^3/h. Analysis of results shows that the presence of the Fe^{3+} catalyst enhances the oxidation rate, which depends on the concentration of the contact, as well as on the pH and the concentration of the suspension. Maximum efficiency of oxidation has been achieved for the 1 wt.% $CaSO_3$ suspension at pH = 5.5 in the presence of the 0.1 wt.% Fe^{3+} catalyst after 1.5 h. The increase of catalyst concentration reduces the duration of the process. The increase of suspension concentration extends the time required for effective oxidation, even though the remaining parameters do not change.

1. INTRODUCTION

Effective and low-waste desulphurization of flue gases (FGD) is an ongoing concern. There are several dozen FGD methods now in use, which have found wide acceptance. Of these, wet regeneration techniques deserve special attention. The majority of wet regeneration processes use calcium compounds to sorb sulphur dioxide. The end product is a low-solubility sediment containing calcium sulphite or

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calcium sulphate. Effluents from sorption which include sulphites are much easier to regenerate than those containing sulphates, because $CaSO_3 \cdot 1/2 \; H_2O$ displays a lower solubility than $CaSO_4 \cdot 2 H_2O$ does. The intermediate product obtained in this way requires further processing in order to improve some of its properties, thus facilitating filtration, storage and future uses. Oxidation of calcium sulphite in solution or suspension yields gypsum as the end-product which may be used as one of the starting compounds for the manufacture of building materials. In this way we shall obtain a no-waste FGD technology.

2. CATALYTIC OXIDATION OF CALCIUM SULPHITE

Experiments on the oxidation of sulphites have been reported in specialized literature a number of times [1]–[3]. Yet, the mechanism governing the process is far from being sufficiently well understood. Literature data, as well as the results reported by the authors of this study [4], indicate that the oxidation rate is noticeably influenced by the presence of the catalyst in the reaction medium. Hence, it may be the ions of the transition metals (Mn, Co, Fe, Cu) that act as catalyst. Their activity depends on the composition of the solution and on the process conditions [5]–[7].

It is a well-established fact that dust particles carried by the flue gas stream exert a catalytic effect on the conversion of sulphites produced during absorption of sulphur dioxide. The transition metals attached to the available surface area of the dust particles make the non-catalytic oxidation of sulphites (in the presence of oxygen contained in the flue gas) run faster [8].

Of the transition metals carried by the flue gas stream, iron content is the highest. It is, therefore, interesting to investigate the catalytic action of Fe^{3+} in FGD processes. For illustration, let us present the content of some metals determined in the flue gas from the manufacture of viscose fibres:

Fe, 8.0 wt.%,   Mn, 0.14 wt.%,
Co, 0.009 wt.%,   Cr, 0.02 wt.%,
Ni, 0.015 wt.%,   V, 0.04 wt.%,
Cu, 0.01 wt.%.

Of the transition metals, the contribution of iron to the efficiency of sulphite oxidation fails to be defined unequivocally [1], [9]–[11]. It was found to vary with each change of the oxidation conditions, and specifically with each change of the oxygen content in the flue gas stream [1] and pH of the solution [12].

To determine the effect of iron on the oxidation of calcium sulphite in suspension in a process involving forced air flow, experiments were run with ferric chloride as a catalyst.

3. EXPERIMENTAL

3.1. EXPERIMENTAL APPARATUS AND MEASURING METHODS

The oxidation of calcium sulphite in suspension was run in a glass reactor with bottom feed of air through a sinter which covered the entire cross-section (12.6 cm^2). A rotameter was used for measuring the air flow rate. Suspensions of 50 cm^3 volume were prepared from laboratory-made $CaSO_3 \cdot 2H_2O$. Calcium sulphite content in the sediment amounted to 68–70 wt.%. The process was carried out at 293 K and an air flow rate of $8.33 \cdot 10^{-6}$ m^3/s. Iron ion concentration in the experimental solutions ranged from 0.01 to 1.0 wt.% in proportion to calcium sulphite. The concentration of the suspension varied from 1 to 5 wt.%. In the course of the oxidation process, 5 cm^3 volume samples of the suspension were collected for analysis at determined time intervals, and pH variations in the solution were measured.

3.2. ANALYTICAL AND CALCULATING PROCEDURES

Suspension samples were analyzed by iodometry for calcium sulphite content, and the efficiency of oxidation was calculated in terms of the following expression

$$U = \frac{(CaSO_3)_i - (CaSO_3)_f}{(CaSO_3)_i} \cdot 100\%$$

where U is efficiency of oxidation (%; $(CaSO_3)_i$ denotes initial calcium sulphite content in suspension (kg/m^3), and $(CaSO_3)_f$ indicates final calcium sulphite content expressed as $CaSO_3$ after a fixed time of oxidation (kg/m^3).

The course of the oxidation process was influenced by the following parameters: time of oxidation (t), concentration of the catalyst (c_c), initial pH, and suspension concentration (c_s).

4. RESULTS AND DISCUSSION

The results obtained are shown in tables 1–5 and in figures 1–5. Thus, table 1 and figure 1 illustrate the effect of pH on oxidation efficiency variations with time. Calcium sulphite was oxidized in the absence of Fe^{3+}. Suspension concentration varied from 1 to 3 wt.%, and pH fell in the range of 4.5–7.0. The pH range had been established from relevant data for the process of SO_2 sorption. Sulphur dioxide sorption is generally run to the pH range of 4.0–4.5, justified by the efficiency of the process and, on the other hand, by the desorption of carbon dioxide which is sorbed together with sulphur dioxide. Furthermore precipitation of calcium sulphate is effective when conducted in an acidic medium.

Table 1

Oxidation efficiency as a function of time (t), suspension concentration (c_s) and pH. Initial concentration of $CaSO_3$ equals 75%

| c_s wt.%	pH = 6.9				pH = 4.5				pH = 5.5			
	t min	pH	$(CaSO_3)_f$ kg/m^3	U %	t min	pH	$(CaSO_3)_f$ kg/m^3	U %	t min	pH	$(CaSO_3)_f$ kg/m^3	U %
1	30	6.3	6.86	8.5	40	4.4	5.03	32.9	40	5.3	5.38	28.3
	60	5.8	6.21	17.2	80	3.6	3.82	49.0	80	5.03	1.01	86.5
	90	–	6.14	18.1	130	3.7	2.03	72.9	130	4.2	0.66	91.2
	120	5.9	6.22	17.1	170	3.9	0.94	87.5	170	4.15	0.55	92.7
	150	–	6.19	17.5								
	180	–	5.96	20.4								
3	45	6.95	21.86	5.2	30	4.65	21.47	4.6	30	5.3	16.31	22.5
	90	6.95	20.37	9.47	60	4.7	16.63	26.1	60	5.32	16.00	28.9
	135	7.05	20.92	7.02	90	4.7	11.19	50.3	90	5.4	14.56	35.3
	180	6.85	20.92	7.02	120	4.4	4.59	79.6	120	5.35	13.50	40
	220	6.95	20.37	9.47	150	4.3	3.28	85.4	150	5.3	11.31	49.8
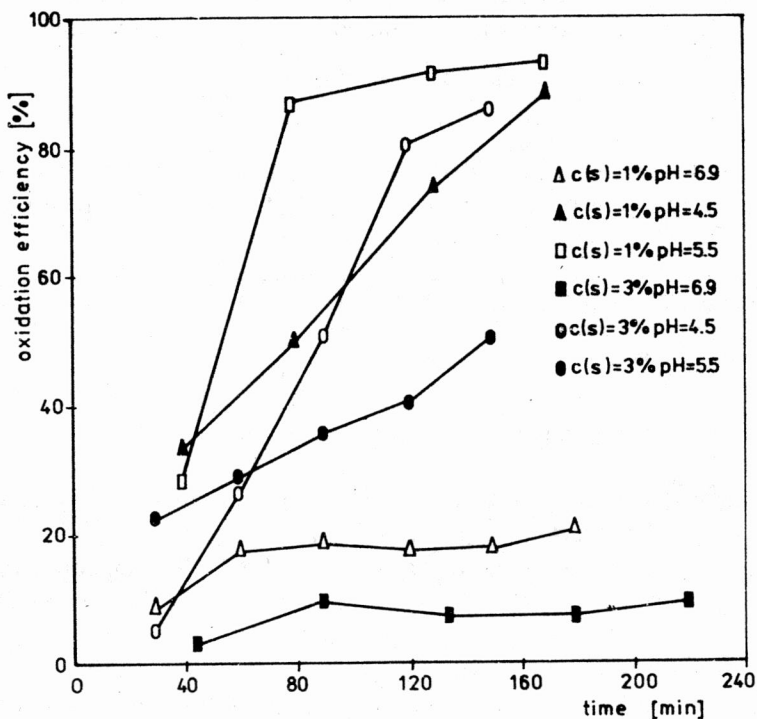
Fig. 1. Effect of pH on oxidation efficiency

Experimental data show that pH has a substantial influence on the efficiency of calcium sulphite oxidation. A 1 wt.% suspension of pH = 5.5 yielded an oxidation efficiency of 86.5% after 80 min. When the concentration of the suspension increased, maximum efficiency was achieved at pH = 4.5. However, after 80 min the efficiency value dropped to 45.0%. When pH amounted to 6.9, the efficiency of oxidation approached 9% and 20% in the 3 wt.% suspension and 1 wt.% suspension, respectively, after a time span of 1.5 h.

The effect of pH on the oxidation rate depends on the solubility of the calcium sulphite sediments, which increases as the pH of the solution decreases. The increase in the measured oxidation efficiency values should also be attributed to the desorption of SO_2, which sets on at pH $\sim$ 4. In solutions with pH = 4.5, there may appear a temporary decrease in the oxidation efficiency value and, also, a loss of SO_2 as a result of sulphite decomposition. Apart from some other contribution factors, the drop of pH to the range of 4.5–5.5 creates favourable conditions for the oxidation of calcium sulphites. Taking into account the potentiality for SO_2 desorption, it is advisable to conduct the oxidation process at pH = 5.5.

Addition of Fe^{3+} (in amounts varying from 0.01 to 0.05 wt.%) to the calcium sulphite suspension at pH = 7 failed to improve the efficiency of oxidation within 2.5 h. A slight improvement (amounting to 10%) was achieved with a catalyst dose increased to 0.1 wt.% of Fe^{3+}. More details are available in table 2 and figure 2.

Table 2

Oxidation efficiency as a function of time (t) and Fe^{3+} concentration (c_c). At constant pH (pH = 7) and constant suspension concentration ($c_s = 1$ wt.%); initial concentration of $CaSO_3$ equals 75%

	$Fe^{3+} = 0.01$ (wt.%)				$Fe^{3+} = 0.05$ (wt.%)			$Fe^{3+} = 0.1$ (wt.%)	
t min	pH	$(CaSO_3)_f$ kg/m^3	U %	pH	$(CaSO_3)_f$ kg/m^3	U %	pH	$(CaSO_3)_f$ kg/m^3	U %
30	6.95	6.75	10	6.90	6.44	14.1	6.70	6.09	18.8
60	6.90	6.63	11.6	6.75	6.19	17.5	6.55	5.81	22.5
90	6.80	6.28	16.3	6.40	6.09	18.8	6.50	5.32	28.7
120	6.75	6.20	17.3	6.25	5.85	22.0	6.45	4.72	37.1
150	6.70	5.97	20.4	5.60	5.55	26.0	6.40	4.49	40.1

The efficiency of oxidation improves noticeably at catalytic enhancement with Fe^{3+} in amounts between 0.05 and 0.1 wt.%, and at pH between 4.5 and 5.5, when the suspension concentration falls between 1 and 3 wt.%. With decreasing pH the efficiency of oxidation increases. This increase is greater at pH = 5.5 (table 3, figure 3).
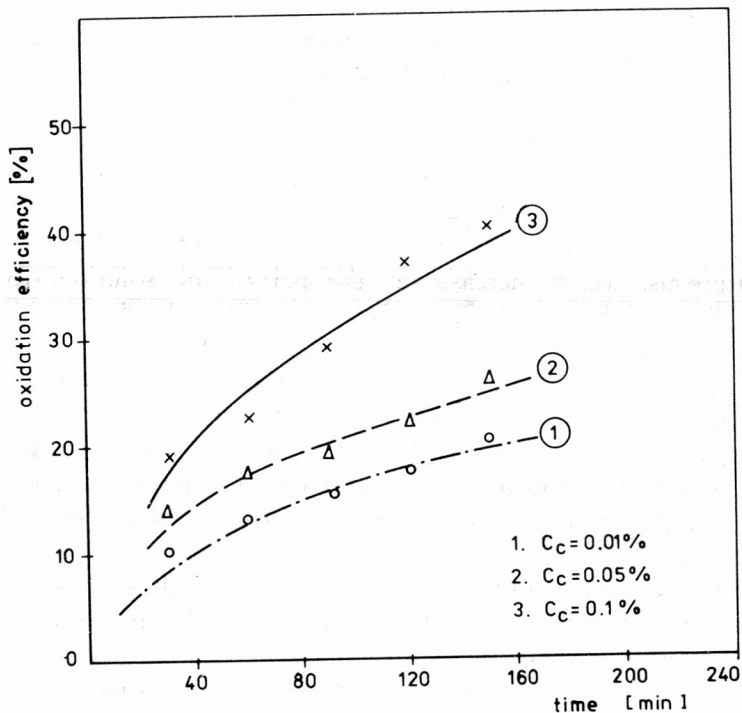
Fig. 2. Effect of Fe^{3+} catalyst on oxidation efficiency (pH = 7)

Complete oxidation of sulphites was achieved after nearly 1.5 h in a 1 wt.% suspension treated with 0.1 wt.% Fe^{3+}. Increase in suspension concentration, decrease of pH to the level of 4.5, and the reduction of the catalyst to one half of the initial value extended the time required to achieve complete oxidation. Based on the data of table 3 and figure 3, we can see that the efficiency of oxidation is primarily influenced by pH and suspension concentration. The effect of the catalyst dose applied is less pronounced.

Taking into account the pH-dependence of the oxidation effect, the process was run for 50 min with a 1 wt.% suspension, a constant catalyst dose (0.1 wt.% Fe^{3+}), and a variable pH (from 4 to 7). Every 10 min, pH and sulphite content in the suspension were measured. The results are included in table 4 and figure 4. As shown by these data, the highest oxidation efficiencies approached 70% and 80%, and were obtained at pH = 4.5 and pH = 5.0, respectively, after only 20 min. At pH = 5.5, oxidation amounted to 87%. When pH fell below, or increased above, this range, the oxidation efficiencies achieved after 20 min were much lower.

The oxidation time of 20 min and the pH level of 5.5 were adopted to investigate the efficiency of oxidation for calcium sulphite suspensions of higher concentration (between 3 and 5 wt.%), treated with higher amounts of Fe^{3+} (varying from 0.1 to 1.0 wt.%

Oxidation efficiency as a function of time (t), suspension concentration (c_s), catalyst concentration (c_c) and pH. Initial concentration of $CaSO_3$ equals 75%

| c_s % | t min | $Fe^{3+} = 0.10$ (wt.%) | | | | | | $Fe^{3+} = 0.05$ (wt.%) | | | | | |
| | | pH = 4.5 | | | pH = 5.5 | | | pH = 4.5 | | | pH = 5.5 | | |
		pH	$(CaSO_3)_f$ kg/m^3	U %	pH	$(CaSO_3)_f$ kg/m^3	U %	pH	$(CaSO_3)_f$ kg/m^3	U %	pH	$(CaSO_3)_f$ kg/m^3	U %
1	30	4.05	2.93	69.0	4.6	0.60	92.0	4.05	3.12	56.4	4.2	2.89	61.5
	60	3.85	1.05	86.0	4.05	0.16	97.9	3.09	2.07	72.4	4.15	1.21	83.9
	90	3.60	0.84	94.6	4.00	0.0	100.0	3.85	1.05	86.0	4.10	0.08	98.9
	115	3.45	0.0	100.0	3.85	0.0	100.0	3.50	0.5	93.3	3.9	0.0	100.0
	145	—	—	—	—	—	—	3.20	0.0	100.0	—	—	—
3	30	4.15	19.52	15.2	4.95	13.23	34.2*						
	60	3.6	10.97	51.2	4.50	7.59	62.2*						
	90	3.4	6.83	69.6	3.95	5.8	74.1*						
	120	3.25	4.48	80.1	3.30	2.19	89.1*						
	150	3.15	2.27	89.9	3.00	0.64	96.8*						

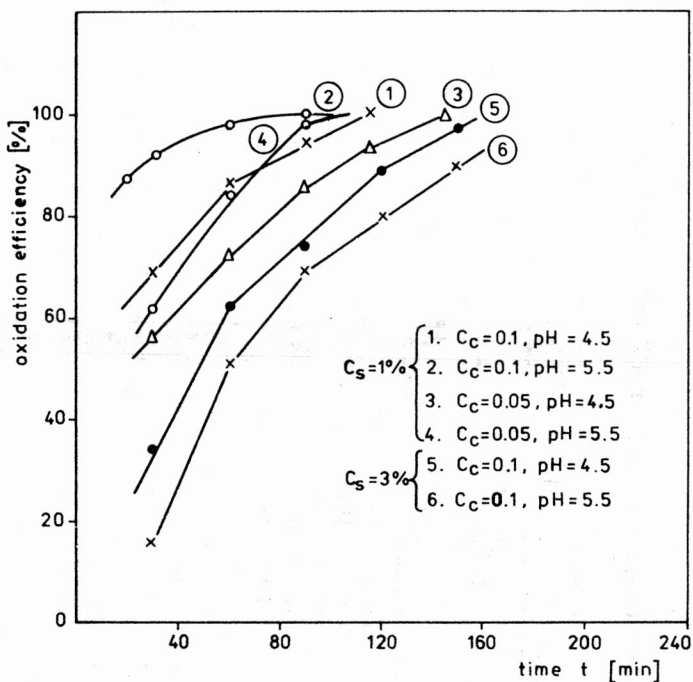* Initial concentration of $CaSO_3$ equals 67%.

Fig. 3. Effect of Fe^{3+} catalyst on oxidation efficiency (pH = 4.5 to 5.5)
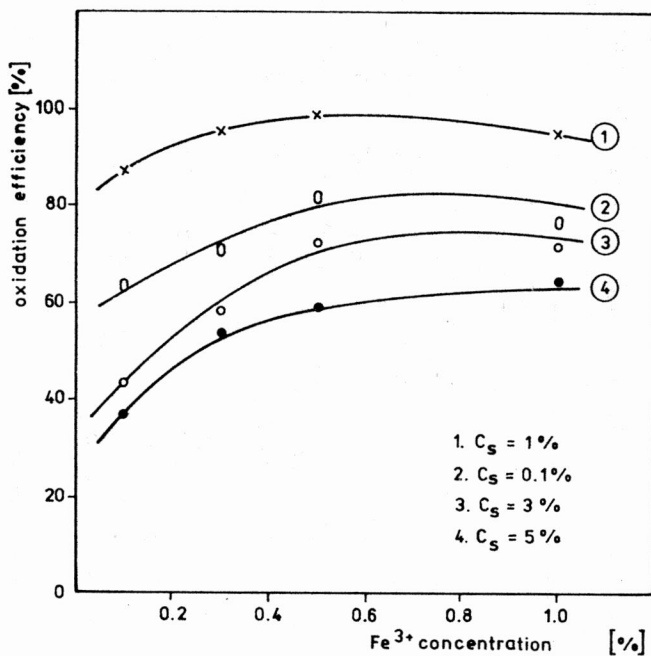

Fig. 4. Effect of pH on oxidation efficiency in the presence of Fe^{3+}
(at constant concentration of 0.1 wt.%)

Table 4

Oxidation efficiency as a function of pH. Experimental conditions: pH = 4 to 7; t = 50 min; c_s = 1 wt.%; c_c = 0.1 wt.%; $(CaSO_3)_i$ = 67%

| t min	pH = 4.0–3.6		pH = 4.5–3.9		pH = 5.0–4.05		pH = 5.5–4.2		pH = 6.0–4.9		pH = 6.5–5.3		pH = 7.0–6.2	
	$(CaSO_3)_f$ kg/m^3	U %	$(CaSO_3)_f$ kg/m^3	U %	$(CaSO_3)_f$ kg/m^3	U %	$(CaSO_3)_f$ kg/m^3	U %	$(CaSO_3)_f$ kg/m^3	U %	$(CaSO_3)_f$ kg/m^3	U %	$(CaSO_3)_f$ kg/m^3	U %
10	3.63	44.8	3.51	47.6	3.31	50.6	2.01	70	4.68	30.1	5.52	17.6	5.54	17.3
20	2.46	63.3	2.22	66.9	1.30	80.6	0.84	87.4	2.91	56.5	5.47	18.4	5.39	19.5
30	1.52	77.3	1.05	84.3	0.55	91.8	0.33	95.0	1.99	70.3	5.21	22.2	5.0	25.5
40	0.62	90.7	0.47	93.0	0.114	98.3	0.21	96.8	1.37	79.5	5.18	22.7	5.0	25.4
50	0.43	93.6	0.04	99.4	0.027	99.6	0.10	98.5	1.13	83.1	5.16	22.9	4.92	26.6
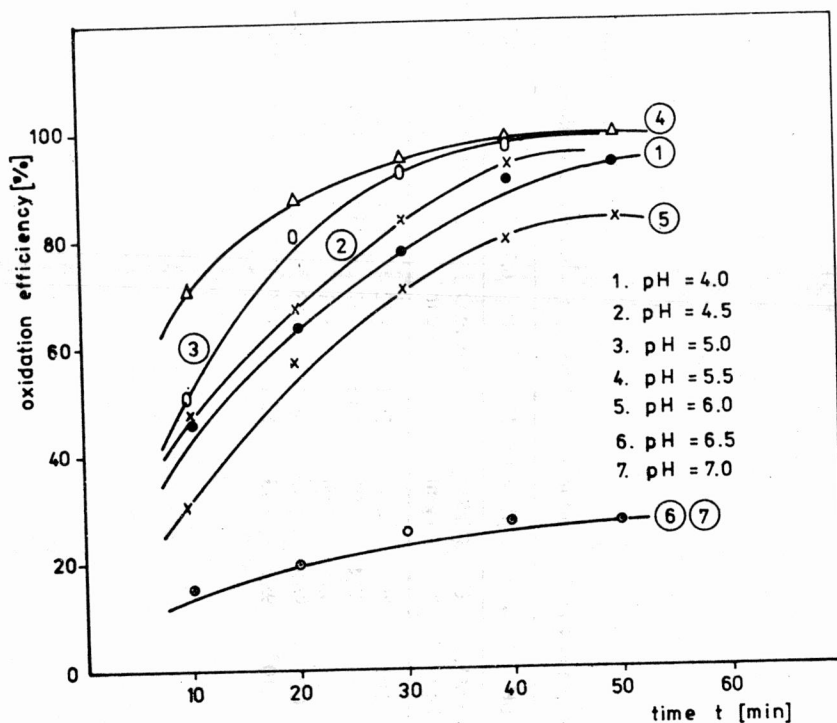
Fig. 5. Effect of Fe^{3+} on oxidation efficiency (at pH = 5.5 and suspension concentration of 1 to 5 wt.%)

in proportion to $CaSO_3$). More detailed information is contained in table 5 and figure 5. These data show that, as the concentration of the calcium sulphite suspension increases from 1 to 5 wt.%, the efficiency of oxidation decreases. When the amount of Fe^{3+} increases, so does the oxidation efficiency, until the maximum value (at $c_c = 0.5$) is achieved. From there, the efficiency value continues to decrease. This finding holds for

Table 5

Oxidation efficiency as a function of Fe^{3+} concentration. Experimental conditions: $c_s = 1$ to 5 wt.%; $c_c = 0.1$ to 1.0 wt.%; $t = 20$ min; pH = 5.5; $(CaSO_3)_i = 67\%$

c_c wt.%	$c_s = 1$ (wt.%)			$c_s = 3$ (wt.%)			$c_s = 5$ (wt.%)		
	pH_f	$(CaSO_3)_f$ kg/m³	U %	pH_f	$(CaSO_3)_f$ kg/m³	U %	pH_f	$(CaSO_3)_f$ kg/m³	U %
0.1	4.20	0.845	87.4	4.5	11.47	42.9	4.8	21.15	36.8
0.3	2.80	0.273	95.9	4.3	8.40	58.2	4.7	15.69	53.2
0.5	2.35	0.039	99.4	4.0	5.62	72.0	4.55	13.9	58.5
1.0	3.70	0.35	94.8	4.8	5.83	71.0	4.65	11.9	64.5

suspension concentrations which fall within 1 and 3 wt.%. No maximum has been measured for the 5 wt.%. concentration. This lack should be attributed to the duration of the process or to the catalyst dose, as either of them is likely to be insufficient to yield a maximum during 20 min.

It is interesting to note that the pH of the solutions shows a tendency to decrease with the increasing efficiency of oxidation. This behaviour is associated with the mechanism governing the process.

5. CONCLUSIONS

1. Oxidation of sulphites is pH-dependent; it increases with the decreasing pH of the solution to reach a maximum at $pH = 5.5$.

2. When the sulphite suspension has a pH approaching 7, no increase in the efficiency of the oxidation process is observed, despite the catalytic enhancement with Fe^{3+}.

3. In the presence of the Fe^{3+} catalyst, there is an increase in the oxidation rate, which depends on the concentration of the calcium sulphite suspension.

4. Maximum efficiency of oxidation 87% has been achieved for a 1 wt.% suspension at $pH = 5.5$, in the presence of a 0.1 wt.% Fe^{3+} catalyst, after 20 min. The time required to obtain complete oxidation amounted to 90 min.

5. When suspension concentration increases from 1 to 5 wt.%, oxidation efficiency decreases. Increasing Fe^{3+} concentration in the catalyst to about 0.5 wt.% accounts for an appropriate increase in the oxidation of calcium sulphite.

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UTLENIANIE SIARCZYNU WAPNIOWEGO POCHODZĄCEGO Z ODSIARCZANIA GAZÓW ODLOTOWYCH W OBECNOŚCI KATALIZATORA ŻELAZOWEGO

Utlenianie siarczynów powstających w procesie odsiarczania gazów odlotowych jest jednym z ważniejszych etapów tego procesu. Stopień utlenienia siarczynów wapniowych wytworzonych w procesie sorpcji SO_2 z zastosowaniem związków wapnia decyduje o jakości, a więc o możliwościach wykorzystania gipsu. Efektywność utleniania zależy od wielu czynników, wśród których na uwagę zasługuje odczyn utlenianego roztworu i obecność katalizatora w środowisku reakcji. Pierwiastkiem z grupy metali przejściowych, najczęściej występującym w środowisku utleniania siarczynów, jest żelazo. Dlatego też podjęto badania nad wpływem żelaza na stopień utleniania siarczynu wapniowego. Na podstawie wyników badań utleniania zawiesiny $CaSO_3$ o stężeniu 1–5% mas. w temperaturze 293 K strumieniem powietrza o natężeniu przepływu $8,33\cdot10^{-6}$ m^3/h ustalono, że pod wpływem Fe^{3+} rośnie prędkość utleniania siarczynów zależnie od stężenia katalizatora, odczynu i stężenia zawiesiny.

Maksymalne wartości stopnia utlenienia uzyskano po 1,5 h utleniania zawiesiny o stężeniu 1% i pH 5,5 w obecności 0,1% Fe^{3+}. Wzrost stężenia katalizatora skraca czas utleniania, a wzrost stężenia zawiesiny wydłuża ten czas przy pozostałych parametrach stałych.

ОКИСЛЕНИЕ СУЛЬФИТА КАЛЬЦИЯ, ПРОИСХОДЯЩЕГО ИЗ ОБЕССЕРЕНИЯ ОТХОДЯЩИХ ГАЗОВ В ПРИСУТСТВИИ ЖЕЛЕЗНОГО КАТАЛИЗАТОРА

Окисление сульфитов, образующихся в процессе обессерения отходящих газов является одним из важнейших этапов этого процесса. Степень окисления сульфитов кальция, произведенных в процессе сорбции SO_2 с применением соединений кальция, решает о качестве, а затем о возможностях использования гипса. Эффективность окисления зависит от многих факторов, среди которых на внимание заслуживает реакция окисляемого раствора и наличие катализатора в среде реакции. Элементом из группы переходных металлов, чаще всего выступающим в среде окисления сульфитов является железо. Поэтому были предприняты исследования влияния железа на степень окисления сульфита кальция. На основе результатов исследований окисления суспензии $CaSO_3$ концентрации 1–5% масс, в температуре 293 К, потоком воздуха интенсивности течения $8,33 \times 10^{-6}$ $m^3/ч$ было установлено, что под влиянием $Фе^{3+}$ растет быстрота окисления сульфитов зависимо от концентрации катализатора, реакции и концентрации суспензии.

Максимальные значения степени окисления были получены после 1,5 ч окисления суспензии концентрации 1% и pH 5,5 при наличии 0,1% Fe^{3+}. Повышение концентрации катализатора сокращает время окисления, а повышение концентрации суспензии протягивает это время при постоянных остальных параметрах.