Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 5, Part 1
ISSN 1313-2539, Published at: http://www.science-journals.eu

OXIDATION OF $CaSO_3$ BY AIR IN THE TECHNOLOGY FOR PURIFICATION OF FLUE GASES FROM SO_2

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Abstract

The presented investigations are connected with creation of a new suitable for small and middle capacity boilers technology for removal of SO_2 from flue gases by absorption with $CaCO_3$ slurry, producing gypsum for building material. To reduce the capital investments it was decided to eliminate the hydrocyclone block and the centrifuge of the existing technologies and to dry the slurry of $CaSO_4.2H_2O$ directly in a spray dryer by flue gases, utilizing the heat of evaporation in a contact economizer system. This decision required practically full oxidation of the $CaSO_3$ to $CaSO_4$ in the oxidizer. A construction of a new oxidizer, divided by vertical partitions into 4 chambers with regular distribution of the air in the slurry by means of perforated horizontal tubes, is described. Some possibilities for cleaning of the orifices of the tubes are specially investigated and a solution is found. It is shown that at presence of catalysts, Fe and Mn ions, more than 99% of the slurry can be oxidized in 9 hours. The obtained after the drying of the slurry gypsum is white. The test of its compressive strength shows a value of 3.5 MPa, i.e. 40% higher than the requirements of the Bulgarian national standard for building gypsum. The obtained data are used for designing the oxidizer of an industrial installation for purification of flue gases from SO_2.

Key wards: *purification of flue gases, SO_2.removal, absorption degree, new technology, catalyst, $CaSO_3$ oxidation, slurry, gypsum compressive strength.*

1. INTRODUCTION

The gypsum technology is the most widely used process for purification of flue gases from SO_2 [1-10]. The typical technological scheme includes an absorber, where the SO_2 from the flue gases is absorbed by slurry of $CaCO_3$ to $CaSO_3$, an oxidizer, where the obtained $CaSO_3$ is oxidized by air to $CaSO_4$, respectively $CaSO_4.2H_2O$, and a dryer for transforming the $CaSO_4.2H_2O$ into $CaSO_4.0.5H_2O$ (building gypsum). The disadvantages of the existing technology are:

1. It is created only for big capacity boilers because their absorbers are high, about 20-30 m and the necessary capital investments are unacceptably great for small and middle capacity boilers.

2. The absorption degree is not high enough – about 95%. It means that about 5% of the initial SO_2 is exhausted in the atmosphere with cooled flue gas, and that is why with poor spreading ability and high concentration in the atmosphere.

The stringent regulations for the maximal permissible concentration of SO_2 in the purified flue gases, connected with the membership of Bulgaria in EU and their continuous tightening call for better solving of the problem. That is why the National Science Fund of Bulgaria in partnership with Trade and technology joint-stock company – Bulgaria funded a project for creation of an installation proper

for small and middle capacity boilers. A part of these investigations is connected with creating of a unit for oxidation of the $CaSO_3$ and drying of the product to gypsum for building purposes. In the present paper the results of this investigation are presented.

2. PROBLEM STATEMENT

According to the literature [3, 4, 11-14] the $CaSO_3$ obtained by absorption of SO_2 in $CaCO_3$ slurry is oxidized by oxygen (air) to $CaSO_4.2H_2O$. The chemical reactions connected with sulfite oxidation, which begin in the SO_2 absorber and finish practically in the oxidizer, are as follows:

$$CaSO_3 + 0{,}5O_2 + 2H_2O = CaSO_4.2H_2O \quad (1)$$

$$SO_2(aq) + H_2O = H_2SO_3 \quad (2)$$

$$H_2S0_3 = H^+ + HSO_3^- \quad (3)$$

$$HSO_3^- + 0{,}5O_2 = HSO_4^- \quad (4)$$

$$HSO_4^- = H^+ + SO_4^{2-} \quad (5)$$

$$HSO_4^- + CaCO_3 = CaSO_4 + HCO_3^- \quad (6)$$

$$HCO_3^- = CO_2 + OH^- \quad (7)$$

$$OH^- + H^+ = H_2O \quad (8)$$

$$CaSO_3 + H_2SO_3 = Ca(HSO_3)_2 \quad (9)$$

$$2HSO_4^{'} + Ca^{++} + 2H_2O = CaSO_4.2H_2O + H_2SO_4 \quad (10)$$

$$H_2SO_4 + CaCO_3 + H_2O = CaSO_4.2H_2O + CO_2 \quad (11)$$

The reactions (2) and (3) take place only in the absorber and all other in both the absorber and the oxydizer. Because of extremely low solubility of the $CaSO_3$, reaction (1) takes place practically only in the solid phase and that is why its rate is diffusion limited and low. The reaction (4) is the main reaction of the oxidation and takes place in the liquid phase. Because the concentration of the HSO_3^- increases with reduction of pH, the reaction rate also increases with reduction of pH.

For calculation of the reaction rate of the sulfite oxidation at 25°C and pH equal to 7.5 and 9 in [15] and [16] the following equation is presented:

$$r = Kc_M^{1/2}c_{S(IV)}^{3/2}\ , \quad (12)$$

where r is in mol per unit of time in unit of reaction volume, K is the kinetic constant and $c_{S(IV)}$ the total sulfite concentration. At 25°C the value of K is between 2 x 10^6 и 36 x 10^6 m^3/mol.s, depending strongly on the composition of the liquid phase, the concentration of the oxygen and pH. Even traces of catalysts such as Co^{2+}, Cu^{2+}, Mn^{2+} and Fe^{2+} and inhibitors, like alcohols, phenols and xydrohinon [17] change strongly the reaction rate. The equation (12) is obtained accepting that the reaction of oxidation is carried out by the chain mechanism of Bäckstrom, where the free radicals which initiate the chain are generated by a reaction with the metallic impurities present in the solution, or by the

action of UV radiation. [18, 19]. According to the investigation [20], the reaction is of a zero-order in oxygen and its rate can be determined by the equation:

$$r = K.c_{HSO_3^-} . \quad (13)$$

The distribution of the air in the apparatuses for oxidation of the $CaSO_3$ slurry in the existing installations takes place by means of a system of agitators. This system has one advantage and two disadvantages in comparison with the air feeding by means of evenly distributed small orifices, never employed in this case up to now. The advantage, which determines the use of agitators in all existing installations, is that they have no problems with fouling. The first disadvantage is the great energy consumption of the agitators. The second is the constant value of pH of the slurry distributed on the absorber cross section, independent of the concentration of SO_2 in the entering flue gas. This leads to reduction of the driving force in the absorber and thus to reduction of its efficiency.

In the existing installations the $CaSO_4.2H_2O$ is separated from the slurry by means of a hydrocyclone block for preliminary separation of the bigger crystals and a following centrifuge for separation of the solution after the hydrocyclone block. The advantage of this type of operation is that the concentration of the sulfites in the oxidized slurry remains constantly high, which leads to increasing of the oxidation rate. On the other hand this leads to irrigation of the absorber by slurry with lower value of pH, which results in reduction of the driving force of the absorption process and thus to reduction of the absorption rate.

Another disadvantage of the existing solution is that because of the high capital investments for the centrifuge it is too expensive for small boilers. That is why it was proposed in a previous investigation [21] to oxidize the sulfites in the slurry practically completely and to dry the $CaSO_4.2H_2O$ in an spray dryer without preliminary separation of the liquid phase. This solution is especially proper, also from energy saving point of view, when the heat used for drying is utilized from the flue gases after the filter following the spray dryer by means of a contact economizer system [21].

The references show that there are no reliable data for the oxidation rate which can be used for dimensioning of the proposed oxidizer with air distribution by means of perforated tubes, and especially for determination of the condition at which no fouling can interrupt its normal operation. The necessary data can be obtained only experimentally. On the other hand, it is well known that every 10^{o}C increasing of the temperature leads to 2 - 3 times increasing of the chemical reaction rate. That is why it is expedient to carry out some experiments to examine the possibility to oxidize the $CaSO_3$ in the dryer.

3. INVESTIGATION OF THE OXIDATION OF THE $CaSO_3$ SLURRY IN THE OXIDIZER

3.1. Experimental

The slurry for the oxidation experiments was obtained by precipitation of $CaSO_3$ obtained by the reaction:

$$CaCl_2 + Na_2SO_3 = CaSO_3 + 2NaCl ,$$

separation of the $CaSO_3$ by filtration, washing away the $NaCl$ and acidifying the obtained suspension by 6% solution of H_2SO_3. In Table 1 the data for pH of the suspension as a function of the volume of the added H_2SO_3, is presented.

Table 1. Changing of the pH of 500 g, 20.84 % $CaSO_3$ suspension by adding of 6% solution of H_2SO_3 at a temperature of 45°C.

ml H_2SO_3	1.1	2.15	3.9	6.15	9.3	12.4	15.7	16.3	23.8	32.0
pH	5.73	5.18	4.62	4.20	3.86	3.65	3.46	3.37	3.2	3.1

The experiments were carried out in a Plexiglas reactor with a rectangular cross section 48x50 mm, placed in a thermostat. The height of the slurry in it was 200 mm. The air stream for oxidation was preliminary humidified and heated to the temperature of the oxygen absorption in the reactor. The preliminary experiments were carried out by passing the air through a perforated synthetic resin-bonded paper (SRBP) plate with different diameters of the orifices in the different cases. The results show that after some time of passing of the air, depending on the orifices' diameter, the pressure drop of the oxidizer, respectively of its orifices, abruptly increases (because of fouling of the orifices). The reduction of the pressure drop to its initial value at a given flowrate is possible by washing of the orifices with water. To minimize the necessary quantity of water it was chosen to distribute the air by means of tubes of a 10 mm diameter with orifices on the lower side.

Because in the small experimental reactor it was possible to distribute the orifices uniformly only by a perforated plate, an experiment with a tube was carried out to test the possibility for unbroken conducting of the process, expecting smaller oxidation rate. In an industrial reactor the orifices are uniformly distributed by applying both types of air distributors.

Since the increasing of pH of the slurry, due to desorption of SO_2, leads to reduction of the oxidation rate, in every 30 minutes pH was corrected to its initial value by adding of 6% solution of H_2SO_3. The temperature was maintained constant by a thermostat. For intensifying the oxidation process, the catalytic effect of different metal ions described in the literature [15, 17, 22] is tested. The best results are obtained with a mixture of $MnSO_4$ and $Fe_3(SO_4)_2$ solution in a ratio of *Mn* to *Fe* about 4:1, which according to the literature data has the greatest synergistic effect. In case of a mixture of *Mn* and *Fe* ions the catalyst was prepared by solution in water of 3.569 g $Fe_2(SO_4)_3.7H_2O$ plus 7.883 g $MnSO_4$ plus 0.3 ml concentrated H_2SO_4 to 50 ml in a graduated flask. The catalyst concentration in this experimental investigation was chosen small enough not to change the white color of the produced dry gypsum.

During the experiments when the applied air distribution device appeared undoubtedly inefficient, to save time the experiment continued with another air distribution device.

3.2. Results and discussion

The experimental conditions and some of the obtained results are presented in Tables 2.1. to 4.2. Under the Tables some comments and details about the experiments are presented.

Explanation of the symbols in the Tables:

τ- time in h;

C- concentration of the $CaSO_3$ in %;

ΔC – changing of the concentration of the $CaSO_3$ in % /h;

ΔP- the pressure drop in mm H_2O column;

V – air flowrate in l/h;

t- temperature in °C;

ISSN 1313-2539, Published at: http://www.science-journals.eu

2 or 3 values separated by "/"of *ΔP and V* –denote values measured before plugging and after cleaning once or twice of the orifices for air distribution at the same other conditions;

Two successive measurements of *ΔP* when a higher value is followed by a low value means that the experiment is continued after cleaning the plugged orifices for air distribution;

2 values separated by "/"of pH - every 30 minutes pH is corrected to its initial value by adding 6% solution of H_2SO_3 , the two values are before and after this correction;

2 or 3 values separated by "/"of *t*- denote measurements at different temperatures, when testing the influence of the temperature on the plugging of the orifices for air distribution;

blank cell– the value is not measured.

Table 2.1. Air distribution by a SRBP plate with 9 orifices with a diameter of 0.7 mm;

Content of *Fe* 0.06 g/l and of *Mn* 0.22 g/l**.**

Experiment No 2.1.

τ **h**	***C*** **%**	***ΔC*** **%/ h**	***pH***	**Δ*P*** **mm *H_2O* *column***	***V*** **l/h**
0	22.54		3.1	580	330
1	20.12	2.42	3.1	620	320
2	17.74	2.38	3.6/3.1	665	320
3	16.24	1.5	3.8/3.1	475	340
4	14.49	1.75	3.5/3.0	650	315
5	12.97	1.52	3.6/3.1	610	315
6	11.84	1.13	3.6/3.1	710	310
7	10.23	1.61	3.6/3.1	710	310
8	9.32	0.91	3.6/3.1	770	310
9	8.93[1]	0.39	3.6/3.1	1090	300
10	7.55	1.38	3.6/3.1	640	350
11	6.26	1.29	3.5/3.1	660	350
12	5.31	0.95	3.5/3.1	645	350
13	4.4	0.91	3.5/3.1	645	350
14	3.55	0.85	3.5/3.1	645	345
15	2.7	0.85	3.4/3.1	635	340
16	2.21	0.49	3.6/3.1	635	340
17	1.01	1.2	3.4/3.1	660	325
18	0.22	0.79	3.2/3.1	640	325
19	0.14	0.08	2.9	640	325

[1] the experiment stopped for unplugging the orifices by washing with water.

Table 2.2. Air distribution by a SRBP plate with 9 orifices with a diameter of 0.7 mm;
Content of *Fe* 0.15 g/l and of *Mn* 0.57 g/l.
Experiment No 2.2

τ	***C***	***ΔC***	***pH***	**Δ*P***	***V***
h	**%**	**%/ h**		**mm H_2O column**	**l/h**
0	15.67		3.1	560	330
1	12.46	3.21	4.9/3.1	610	320
2	9.19	3.27	3.5/3.1	645	320
3	7.21	1.98	3.5/3.1	770	305
4	5.58	1.63	3.5/3.0	870	300
5	3.56	2.02	3.5/3.1	820	320
6	2.57	0.99	4.1	870	310

It can be seen from Table 2.2. that at a lower initial $CaSO_3$ concentration, high content of a the catalyst and a great air flowrate the $CaSO_3$ oxidation rate is relatively high, decreasing with the advance of the oxidation degree. An increase of the pressure drop, owing to plugging of the air distribution orifices, is observed.

Table 2.3. Air distribution by a SRBP plate with 9 orifices with a diameter of 0.7mm;
Content of *Fe* 0.15 g/l and of *Mn* 0.57 g/l
Experiment No 2.3.

τ	***C***	***ΔC***	***pH***	**Δ*P***	***V***
h	**%**	**%/ h**		**mm H_2O column**	**l/h**
0	22.25	-	3.1	460	340
1	18.56	3.69	3.7/3.1	830	300
2*	14.62	3.94	3.6/2.9	1040	285
3	11.64	2.98	3.8/3.05	440	340
4	10.5	1.14	4.5/3.1	650	335
5	7.61	2.89	3.6/3.1	660	325
6	4.65	2.96	3.6/3.1	650	330
7	3.05	1.6	3.5/3.1	655	330
8	1.42	1.63	3.6/3.0	650	325
9	0.22	1.2	2.2	625	350

* plugging of the air distribution orifices between the 2nd and the 3rd hour.

The influence of the catalyst concentration on $CaSO_3$ oxidation rate is presented in Fig. 1.

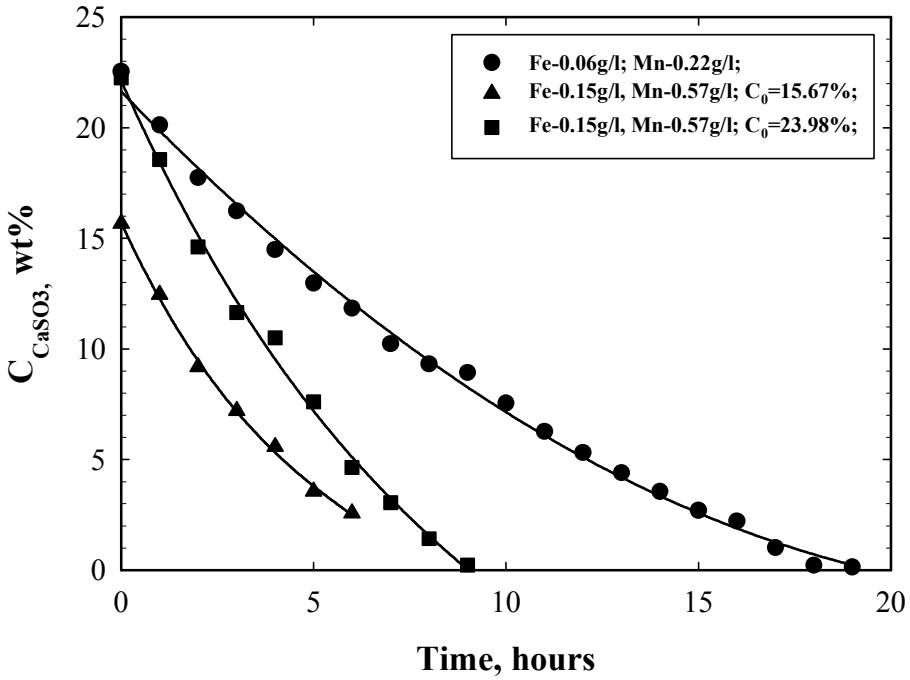


Fig. 1. Influence of the catalyst concentration on $CaSO_3$ oxidation rate (C_o is initial $CaSO_3$ concentration).

Table 3.1. Air distribution by a rubber plate with 9 orifices with a diameter of 1.5 mm; *Fe* 0.06 g/l and *Mn* 0.22 g/l;

Experiment No 3.1.

τ **h**	***C*** **%**	***ΔC*** **%/ h**	***pH***	**Δ*P*** **mm *H_2O column***	***V*** **l/h**
0	24.28		3.1	800	300
1					
2					
3	20.56	3.72	3.4/3.1	1420	250
4	19.74	0.82	3.6/3.1	1200	320
5	17.11	2.63	3.7/3.1	1100	295
6	15.56	1.55	3.4/3.1	980	300
7	14.13	1.43	3.5/3.1	1080	285
8	12.12	2.01	3.8/3.1	1100	280
9	11	1.12	3.5/3.1	1300	265
10	10	1	3.5/3.1	1380	255

ISSN 1313-2539, Published at: http://www.science-journals.eu

11	8.37	1.63	3.5/3.1	1400	250
12	7.17	1.2	3.4/3.1	960	230
13	5.68	1.49	3.7/3.1	345	390
14	5.21	0.47	3.4/3.1	340	395
15	4.51	0.7	3.4/3.1	390	340
16	3.25	1.26	3.5/3.0	330	395
17	1.7	2.35	3.5	335	395

Table 3.2. Air distribution by a teflon plate with 9* orifices with a diameter of 0.7 mm and a teflon tube with 6 orifices with a diameter of 0.7 mm;

Fe 0.06 g/l and *Mn* 0.22 g/l

Experiment No 3.2.

τ **h**	***C*** **%**	***ΔC*** **%/ h**	***pH***	**Δ*P*** **mm *H_2O column***	***V*** **l/h**
0	22.94	-	3	525	250
1	19.26	3.68	3.6/3.1	550	235
2	18.21	1.05	4.0/3.1	670	260
3	15.15	3.06	3.5/3.1	850/615	305
4	11.93	3.22	3.5/3.1	840/670	250
5	11.83	0.1	3.5/3.1	900/580	210
6	10.5	1.33	3.4/3.07	1110/800	195
7	8.62	1.88	3.5/3.1	860/655	205/255
8	6.92	1.7	3.6/3.1	710	350
9	5.66	1.26	3.5/3.1	750/520	100
10	5.36	0.3	3.5/3.1	515	100
11	5.11	0.25	3.5/3.1	490	100
12	4.79	0.32	3.5/3.1	820	100
13	4.67	0.12	3.3/3.1	730	100
14			3.3/3.05	700	100
15			3.3/3.1	760	100
16			3.3/3.1	750	
17			3.3/3.1	1010	
18	2.71	1.96	3.3/3.1	960	100

* At an air flowrate of about 200-250 l/h, 6 orifices are not plugged. The number of the open orifices decreases at a smaller flowrate and increases to the maximal at a greater flowrate.

The Experiment No 3.1, presented in Table 3.1., was conducted with a rubber plate with 9 orifices of about 1.5 mm diameter. It was expected that the vibrations of the elastic plate material would result in self-cleaning of the orifices. This idea was not successful because the orifices were plugged with gypsum between the 7th and 8th hour. After cleaning they were plugged again between the 11th and 12th hour.

The Experiment No 3.2., Table 3.2., started with air distribution by a teflon plate with 9 orifices with a diameter of 0.7 mm. Plugging of the orifices occurred at the 2nd hour. The decrease of the pressure drop to 615 mm H_2O is due to a orifices' cleaning. After the 7th hour the experiment continued with air distribution by a horizontal perforated teflon tube placed diagonally in the reactor. The tube has 6 orifices, 3 on each side. The orifices are with a diameter of 0.7 mm and are bored at an angle of 60 ^{o} directed downwards.

Table 3.3. Air distribution by a teflon plates with 16 orifices with a diameter of 0.4 mm and with 4 orifices with a diameter of 1 mm;

Fe 0.06 g/l and *Mn* 0.22 g/l;

Experiment No 3.3.

τ **h**	***C*** **%**	***ΔC*** **%/ h**	***pH***	**Δ*P*** **mm *H_2O* column**	***V*** **l/h**
0	23.98		3.05	505	105
1	21.96	2.02	3.3/3.12	750	100
2	21.12	0.84	3.3/3.1	950	205
3	19.98	1.14	3.5/3.1	740	160
4	18.2	1.78	3.6/3.05	600/1230	150
5	15.72	2.48	3.3/3.1	700/1070	150
5.5	15.07	0.65	3.6/3.1	490	110
6			3.3/3.05	525	110
6.5	14.46	0.61	3.3/3.1	560	110
7			3.3/3.1	645	105
7.5	13.99	0.47	3.3/3.1	725	100
8			3.3/3.1	890	115
8.5	13.59	0.4	3.2/3.1	970	110
9			3.3/3.1	1100	100
9.5	13.57	0.02	3.8/3.1	550	100
10			3.3/3.1	610	100
10.5			3.3/3.1	1000	110
11			3.3/3.1	1040	105
11.5	7.85	5.72	3.3/3.1	1140	100

14	6.12	1.73	3.4/3.1	610	100
15	5.51	0.61	3.3/3.1	535	110
16	5.31	0.2	3.5/3.1	625	100
17	4.98	0.33	3.4/3.1	680	95
18	4.63	0.35	3.4/3.1	1000	90
19	3.8	0.83	3.3/3.05	600	250
20	3.16	0.64	3.5/3.1	900	225
20.5	1.76	1.4	4.15	1100	190

Experiment No 3.3., Table 3.3., was carried out with air distribution by a teflon plate with 16 orifices with a diameter of 0.4 mm. Because of the many times plugging of the orifices and the sharp increase of the pressure drop after the 5.5 hours, this teflon plate was changed by another with 4 orifices with a diameter of 1 mm. Although the flowrate was increased and the plate orifices were bigger (1 mm diameter), the oxidation rate was low and plugging occurred many times. At the 21.5 hour the experiment was stopped by full plugging of the orifices.

Table 3.4. Air distribution by a teflon plate with 16 orifices with a diameter of 0.4 mm and teflon perforated tubes;

Fe 0.06 g/l and *Mn* 0.22 g/l;

Experiment No 3.4.

τ **h**	***C*** **%**	***ΔC*** **%/ h**	***pH***	**Δ*P*** **mm *H_2O column***	***V*** **l/h**
0	21.24	-	3.5	1240	240
1	19.59	1.65	3.6/3.1	1300	190
2	18.88	0.71	3.7/3.55	1320	190
3.5	17.63	1.25	3.6/3.1	1320	190
4.5	16.12	1.51	3.7/3.5	1440	170
5.5	15.59	0.53	3.7/3.5	1500	160
6.5	14.69	0.9	3.6/3.5	840	230
7.5	13.99	0.7	3.7/3.5	830	220
8.5	12.44	1.55	3.6/3.1	585	190
9.5	11.28	1.16	3.3/3.1	1300/1640	200
10.5	10.46	0.82	3.4/3.1	620	230
11.5	9.43	1.03	3.5/3.1	1200	185
12	-		3.4/3.1	1800	130
12.5	8.82	0.61	4.1/3.5	590	200

16.5			3.6/3.5	980	200
17.5			3.6/3.5	970	195
18.5	8.31	0.51	2.67	730	200
19.5	7.59	0.72	2.86	1600	200
21.5	6.47	1.12	3.6/3.1	1610/615	210/200
23	5.32	1.15	3.7/3.1	630	200
23.5	5.19	0.13	3.1		

Experiment No 3.4., Table 3.4., was carried out with air distribution by a teflon plate with 16 orifices with a diameter of 0.4 mm. Plugging of the orifices occurred during the first half an hour. The experiment was performed at a higher pH and a room temperature of 18-22^{o}C to test the plugging of the orifices. After 8.5 hours the experiment was continued with air distribution by a horizontal teflon tube with a diameter of 10 mm and a wall thickness of 1 mm. It has 6 orifices, 3 on each side. The orifices are with a diameter of 0.7 mm and are bored at an angle of 60 ^{o} directed downwards. At the 18.5 hour the operation was continued in a thermostat at a temperature of 45^{o}C. At the 21.5 hour the experiment continued with air distribution by a horizontal teflon tube with 6 orifices with a diameter of 0.7 mm directed vertically downwards. It was found that this design allowed more effective washing.

Table 3.5. Air distribution by teflon perforated tubes;

Fe 0.06 g/l and *Mn* 0.22 g/l;

Experiment No 3.5.

τ	***C***	***ΔC***	***pH***	***ΔP***	***V***
h	**%**	**%/ h**		**mm H_2O column**	**l/h**
0	25.75		3.1	1000	200
1	22.99	2.76	3.6/3.1	620	235
2	20.43	2.56	3.8/3.1	1080/1560	240
2.5	18.21	2.22	3.7/3.1	1570	215
3.5	16.67	1.54	3.6/3.1	1680	300
4.5	14.21	2.46	3.6/3.1	740	230
5.5	13.39	0.82	3.4/3.1	1010	200
6			3.5/3.1	1150/630	250
7	12.66	0.73	3.5/3.1	780	250
7.5			3.6/3.1	2040/1590	190
8	11.93	0.73	3.5/3.1	970/700	250
9	11.78	0.15	3.5/3.1	720	295
10			3.5/3.1	660	290

11	10.73	1.05	3.5/3.1	1100	240
12	10.27	0.46	3.5/3.1	1200/820	270
13	9.61	0.66	3.5/3.1	1695/730	250
13.5			3.5/3.1	1900/1650	200
14	9.48	0.13	3.5/3.1	560	255
15	8.78	0.7	3.6/3.1	1140/650	250
16	8.25	0.53	3.6/3.1	1260/860	240
17	7.7	0.55	3.3/3.1	725	240
18	6.6	1.1	3.4/3.1	1610	110
19	6.39	0.21	3.6/3.1	670	250
20	5.02	1.37	3.6/3.1	1780/1040	230
22	4.47	0.55	3.5/3.1	960	200
23	4.12	0.35	3.5/3.1	725	220
24	3.69	0.43	3.5/3.1	1840/1320	170

Experiment No 3.5, Table 3.5., started with air distribution by a teflon tube (6 orifices with a diameter of 0.7 mm directed vertically downwards) at 45°C. From the 4.5 hour the experiment continued with two thermostats, one for the air at 60 °C, and the second for the reactor at 45 °C. The aim was to use the water, condensed from the air cooled in the oxidizer, for washing the orifices of the teflon tube. At the 14th hour the air distribution continued by a teflon tube with 6 orifices with a diameter of 0.7 mm, 3 on each side directed downwards at an angle of 60°. Between the 16th and the 17th hour plugging occurred. The orifices were blown through by increasing the air pressure.

Table 3.6. Air distribution by a teflon tube with 6 orifices with a diameter of 0.7 mm directed vertically downwards;

Fe 0.06 g/l and *Mn* 0.22 g/l;

Experiment No. 3.6.

τ **h**	***C*** **%**	***ΔC*** **%/ h**	***pH***	**Δ*P*** **mm H_2O column**	***V*** **l/h**	***t***
0	28.21	0	3.1	1205/600	200	44.5
1	28.01	0.2	3.3/3.1	660	200	40.1
2	27.84	0.17	3.3/3.1	670		37.4
3	27.67	0.17	3.5/3.1	530	200	34.7
4	27.55	0.12	4.0/3.3	565	200	20
4.5			3.5/3.3	940/600	185/210	23
5			3.5/3.3	1700/600	90/200	23
6	27.32	0.23	3.5/3.3	1320/650	150/210	23.1

7			3.5/3.3	910/625	170/210	23.8
8	27.21	0.11	3.5/3.3	1400/630	140/210	23.8
10	26.98	0.23	3.5/3.3	1700/590	80/215	23.8
10.5			3.7/3.3	580	220	25.1
11			3.5/3.3	580	215	25.7
11.5			3.6/3.3	595	215	26.6
12			3.5/3.3	1150/940	190/220	35.5
12.5	21.31	5.67	3.6/3.3	800	215	42.1
13.5	19.53	1.78	3.8/3.1	685/565	220	45
14	17.82	1.71	3.5/3.1	1100/860	200	45/83
15	15.77	2.05	3.5/3.1	940/720	225	46
15.5			3.5/3.1	1390/920	150	44/84.5
16	15.47	0.3	3.72	700	190	44/63
16.5			3.96	780	185	44/63
17	14.69	0.78	3.98	830	180	42/63
17.5			4.0/3.85	1410/780	185	42/63
18	14.12	0.57	3.94	980	170	41/63
18	14.12	0.57	4	720	200	42.5/63
18.5			4	770	200	45.2/63
19			4.3/4.0	1040/610	200	46/63
19.5			4.3	650	200	45./63
20	10.52	3.6	4.7/4.0	850	190	45/63
20.5			4.2	730	195	45/63
21			4.41/4.0	1200/610	200	46/63.5
21.5			4.5/4.0	900	200	44.5/63
22	7.12	3.4	4.6/4.3	1340/680	215	45/63
22	7.12	3.4	4.6/4.1	730	190	45/63
22.5			4.2	770	190	45/66
23			4.4	800	195	44/56.5/66.5
24	5.48	1.64	4.5	810	185	45/56/66.5
24.5			4.6/4.4	820	180	45/56/66.5
25.5			4.6/4.4	930	170	45/56/66.5
26	4.34	1.14	4.7/4.4	730	190	45/56/66.5
26.5			4.3	710	200	45/56/66.5
27			4.75/4.4	800	190	45/60.5/71

27.5			4.4	825	190	45/59.5/70
28	2.18	2.16	4.6/4.4	910	190	45/59.5/70
28.5			4.7/4.4	915	185	45/59.5/70
29	1.39	0.79	4.5	1080	200	45/63/70
29.5			4.6/4.5	1070	200	45/60/69
30	0.72	0.67	4.55	1090	200	45/60/69
30.5			4.6/4.5	1080	200	45/60/69
31	0.36	0.36	2.79	1100	200	45/60/69

In Experiment No 3.6., Table 3.6., the data for the oxidation were obtained at cooling and heating of the reactor with the aim to test the influence of the temperature on the plugging of the orifices. The heating began at the 11.5 hour and at the 12th hour plugging was observed. At a temperature of 85^{o}C of the thermostat for the air, spontaneous unplugging was observed. At the 18th hour the concentration *C* was corrected by compensation of the effect of watering of 70 g/h. At the 22th hour watering of the slurry was observed with 42.5 g/h and the slurry was corrected to the initial volume and catalyst concentration.

Table 3.7. Air distribution by teflon perforated tubes;

Fe 0.06 g/l and *Mn* 0.22 g/l;

Experiment No 3.7.

τ	***C***	***ΔC***	***pH***	**Δ*P***	***V***	***t***
h	**%**	**%/ h**		**mm *H_2O column***	**l/h**	
0	22.37	0	3.5	670	220	44/55/69
0.5			3.8/3.5	940	180	45/53/69
1			3.8/3.5	1130	170	45/51/69
2	19.8	2.57	3.8/3.5	1570	100	45/28/69
2			3.9/3.5	690	200	45/59/69
2.5	18.53	1.27	3.8/3.5	1150/790	200	45/56/69
3			3.6/3.5	820	230	45/54/69
3.5	16.6	1.93	3.9/3.5	570	230	45/59/69
4			3.8/3.5	590	220	45/58/69
4.5			3.8/3.5	600	200	45/58/69
5			4.1/3.5	630	210	45/59/69
5.5			3.9/3.5	665	230	45/59/69
6	15.91	0.69	04.3.2005	610	230	45/59/69
6.5			3.8/3.5	620	230	45/60/69

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7			3.9/3.5	635	220	45/59/69
7.5	14.38	1.53	3.9/3.5	630	210	45/58/69
7.5	14.38	1.53	3.5	820	195	45/56/69
8			3.75/3.5	715	210	45/56/69
8.5	13.87	0.51	3.85/3.5	630	210	45/57/69
9			3.8/3.5	635	210	45/57/69
9	13.02	0.85	3.9	790	200	45/55/69
9.5			3.9	590	220	45/57/69
10	12.56	0.46	3.9	705	200	45/56/69
11	11.48	1.08	4.3/3.95	800	200	45/56/69
11.5			4.2/3.95	825	200	45/56/69
12	10.13	1.35	4.2/4.0	910	190	45/55/69
12.5			4.2/4.0	1240	150	45/51/69
13	8.92	1.21	4.15/4.0	1150	165	44/49/69
13.5	7.35	1.57	4.3/4.0	920	260	45/60/69
13.5			4.3	680	300	46.8/62/69
14.5	6.55	0.8	4.8/4.5	740	310	49.5/62.5/69
15.5			4.8/4.5	735	305	47.5/62/69*
17.5			4.9/4.5	620	315	45/58.5/69
18			5	685	300	45/62/69
18.5	5.04	1.51	4.5	770	300	45/61/69
19.5			4.6/4.5	735	300	45/62/69
20	4.24	0.8	4.7/4.5	745	300	45/62.5/69
20.5			4.7/4.5	760	300	45/62/69
21	3.32	0.92	4.7/4.5	720	300	45/62.5/69
21.5			4.6/4.5	720	310	45/62/69
22	2.28	1.04	4.6/4.5	720	300	45/62/69

In Experiment No 3.7., Table 3.7, at the 2nd hour plugging was observed. The data presented were obtained after cleaning the tube orifices. At the 5th hour an average slurry watering of 34 g/h was observed and compensated. At the 7th hour the probe is concentrated by decantation as in the previous cases. An average watering of 72.5 g/h was observed. From the 13.5 hour the air flowrate was increased to about 300 l/h, to test the possibility for self-cleaning of the orifices (47.5/62/69*, room temperature 16 °C). An average watering of 65 g/h was observed.

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Table 3.8. Air distribution by teflon and steel perforated tubes covered with a hydrophobic membrane; *Fe* 0.06 g/l and *Mn* 0.22 g/l;
Experiment No 3.8.

τ	***C***	***ΔC***	***pH***	**Δ*P***	***V***	***t***
h	**%**	**%/ h**		**mm H_2O column**	**l/h**	
0	19.55	0	3.1	800	260	45/61/69
1	16.54	3.01	3.9/3.1	1200	210	45/58/69
1.5			3.3/3.1	710	270	45/61/69
2	16.02	0.52	3.25	660	280	45/60/69
3	15.69	0.33	3.9/3.5	1040	225	45/59/69
3.5			3.75/3.5	1180	205	45/58/69
4	15.22	0.47	3.75/3.5	675	280	45/58/69
5			4.1/3.5	770	285	45/62/69
5.5			3.9/3.5	900	260	45/61/69
6	14.57	0.65	3.9/3.5	1230	230	45/60/69
6.5			3.9/3.5	1380	210	45/60/69
7	14.14	0.43	3.9/3.5	1100	210	45/61/69
7.5			3.7/3.5	1300	180	45/56/69
8	13.92	0.22	4.0/3.5	760	300	45/62/69
8.5			3.8/3.5	970	390	45/61/69
9			3..9/3.5	950	275	45/61/69
9.5			4.0/3.5	1020/760		45/59/69
10	9.94	3.98	3.9/3.5	890	275	45/59/69
10	9.94	3.98	3.8/3.5	690	335	45/63/69
10.5			3.9/3.5	770	340	45/61/69
11	9.16	0.78	4.0/3.5	810	270	45/62/69
11.5			3.8/3.5	910	265	45/61/69
12	8.53	0.63	3.9/3.5	1000/710	260	45/61/69
12.5			3.85/3.5	930	260	45/59/69
13	8.05	0.48	4.1/3.5	670	300	45/61/69
13.5			3.9/3.5	730	300	45/63/69
14	6.72	1.33	4.0/3.5	820	300	45/61/69
14.5			4.0/3.5	880	290	45/62/69
15	5.17	1.55	3.9/3.5	900	290	45/62/69
15.5			3.9/3.5	950	275	45/61/69
16	4.16	1.01	3.9/3.5	1100	250	45/61/69

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In Experiment No 3.8., Table 3.8., the system was plugged between the 3.5 and the 4th hour and again between the 7.5 and the 8th hour. An average watering of 70 g/h was observed. Tests were carried out with a perforated teflon and stainless steel tubes covered with a hydrophobic membrane. The obtained results showed very high degree of slurry oxidation. Unfortunately the membrane was covered by gypsum and plugged. Washing was possible only from outside the tube and that was why these experiments were stopped.

The following tests were carried out with the purpose of determining the possibilities for plugging and unplugging of tubes with different perforation. The results are shown in Tables 4.1.and 4.2.

Table 4.1. Air distribution by a horizontal steel tube with 4 orifices with a diameter of 1 mm directed vertically downwards; Fe 0.06 g/l and Mn 0.22 g/l;

Experiment No 4.1.

τ	***C***	***ΔC***	***pH***	**Δ*P***	***V***	**t**
h	**%**	**%/ h**		**mm H_2O column**	**l/h**	
0	12.14		3.1	750	200	45
0.5			3.9/3.1	690	210	47
1			3.9/3.1	760	210	46
1.5			3.8/3.1	930/760	190/210	46
2			3.1	940/760	190/210	46
2.5	7.46	4.68	3.9/3.1	930/690	210	45
3			3.4/3.1	940/740	190/210	43
3.5			3.4/3.1	920/780	190/210	
4.5	5.49	1.97	3.9/3.1	815	200	
5			4.1/3.1	780	210	
6			3.6/3.1	930	200	
6.5	4.66	0.83	3.8/3.1	1050/780	190/210	

Table 4.2. Air distribution by a horizontal steel tube with 6 orifices with a diameter of 0.7 mm directed vertically downwards; Fe 0.06 g/l and Mn 0.22 g/l;

Experiment No 4.2.

τ	***C***	***ΔC***	***pH***	**Δ*P***	***V***	**t**
h	**%**	**%/ h**		**mm H_2O column**	**l/h**	
0	19.96	0	3.5	620	200	37
0.5			3.8	920/670	180/200	43
1			4.4/3.5	790/740	185/200	45
1.5			3.9/3.5	930/740	180/200	45
2			4.0/3.5	770/740	200	45

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2.5	17.27	2.69	4.0/3.5	1230/780	160/200	45
2.5*	17.27	2.69	3.5	605(610)	205	36
3.5			3.9/3.5	775/600	190/210	45
4.5			4.05/3.5	750/610	200/210	45.5
5.5			4.1/3.5	770/610	195/205	45.6
6.0*	15.72	1.55	3.9/3.5	700/610	200/205	45.6
6	15.72	1.55	3.5	695	200	36
7.5			3.9/3.5	750/635	195/210	44
9			4.1/3.5	790/640	195/210	45
10	12.75	2.97	3.9	780/ stop	180	48
10	12.75	2.97	3.5	620	200	30
12			3.9/3.5	800/615	180/200	45
13.5			4.1/3.5	870/670	200/210	45
14.5			4.1/3.5	780	200	45
15	10.27	2.48	4.1/3.5	830	200	44
15	10.27	2.48	3.5	700	200	42.5
16			4.1/3.5	810/620	195/205	46.5
17			4.1/3.5	800/615	195/205	44
18			3.9/3.5	790	200	44
19			3.9/3.5	780	200/205	45
20	5.21	5.06	3.9	780/600	200/215	45

In both experiments, Table 4.1., and 4.2., the procedure was the following. For washing of the tube orifices, pure water was injected with the air every half an hour. The reactor was stopped periodically and after decantation of the slurry the additional water from washing and condensation of the water vapor from the air was removed. It was found by chemical analysis that the water contained no calcium sulfite and bisulfite. The total water flowrate varied between 100 and 140 ml/h. The presented data for the sulfite concentration were obtained from the analysis data recalculated with the increase of the slurry volume due to watering.

In conclusion it was found the following:

1. By injecting water with the air every 30 minutes, the process can be carried out continuously without stopping for cleaning of the tube orifices;

2. The oxidation rate without catalyst is unacceptably low for our technology;

3. At adding of 0.06 g/l *Fe* ions and 0.22 g/l *Mn* ions, over 99% of the slurry have been transformed into gypsum for 19 hours (Fig.1 and Table 2.1, Experiment No 2.1.);

4. At adding of 0.15 g/l *Fe* ions and 0.57 g/l *Mn* ions, over 99% of the slurry have been transformed into gypsum for 9 hours (Fig.1 and Table 2.3., Experiment No 2.3.);

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5. The adding of catalyst in the concentrations given above does not change the white color of the obtained dried gypsum.

3. ABOUT THE QUALITY OF THE OBTAINED GYPSUM

In the following Figures some electron microscope photographs of the obtained gypsum crystals are presented, taken immediately after the oxidation of the slurry, Fig.1, and 40 days after the oxidation of the slurry, Fig. 2.

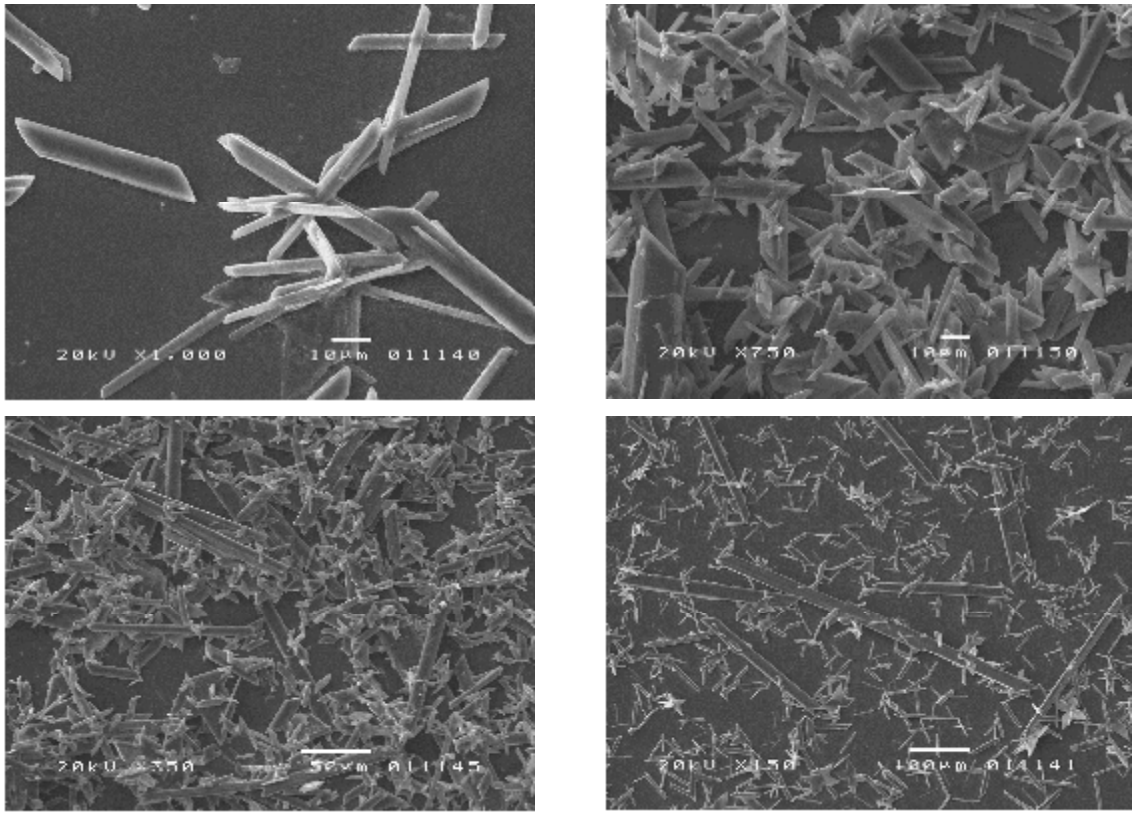


Fig. 1. Gypsum crystals immediately after the oxidation of the slurry

The tests of the compressive strength of the obtained gypsum show a value of 3.5 MPa, i.e. 40% higher than the requirements of the Bulgarian national standard for building gypsum.

The obtained data are used for designing the oxidizer of an industrial installation for purification of flue gases from SO_2.

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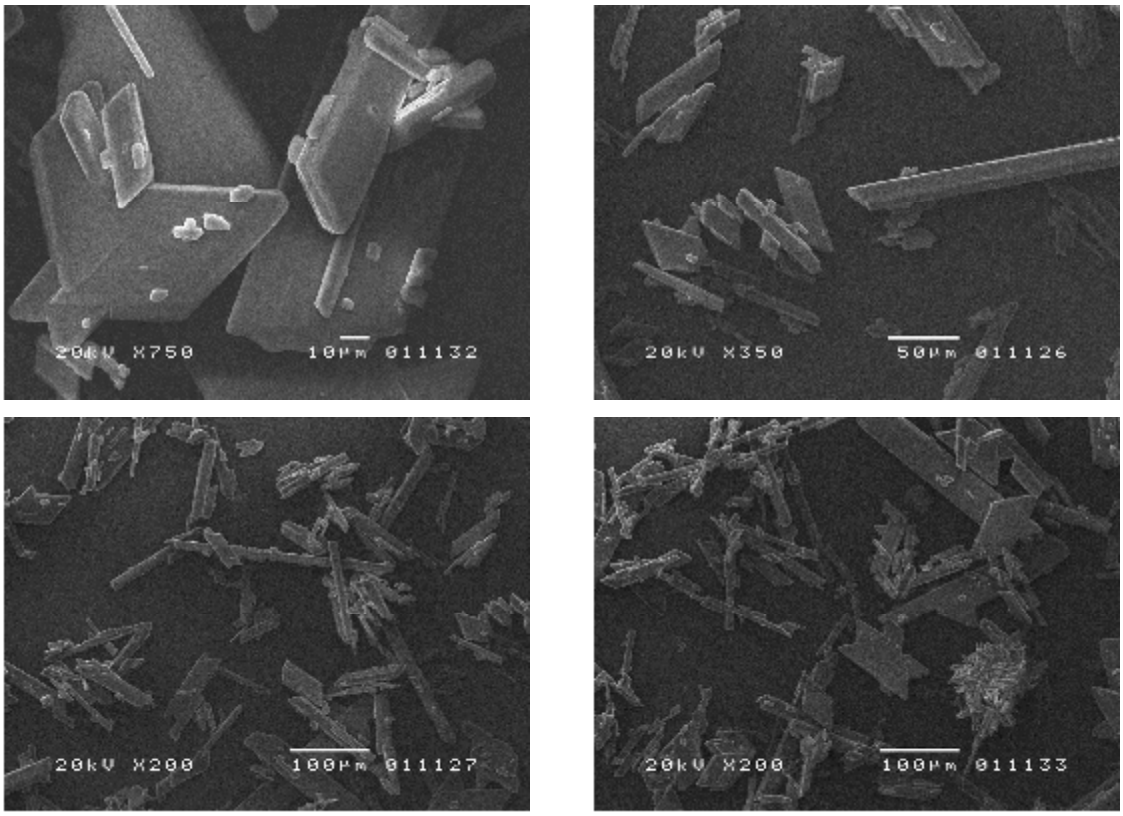


Fig. 1. Gypsum crystals 40 days after the oxidation of the slurry.

4. PRELIMINARY INVESTIGATION FOR OXIDATION OF $CaSO_3$ BY DRYING

Besides in slurry a test oxidation of $CaSO_3$ was also carried out at the temperature of drying. The purpose was to test the possibility for oxidation of $CaSO_3$ dust on the filter after the spray dryer. The experiment was carried out by passing 200 l/h hot air with a temperature 220-230°C trough a layer of a precipitate of $CaSO_3$ on a glass shot filter with a diameter of 40 mm. The result shows that for 2 hours oxidation the transforming of the $CaSO_3$ into $CaSO_4$ was only 26.4%, i.e. insufficient to make this possibility of oxidation perspective from economical point of view.

5. CONCLUSION

A construction of a new oxidizer, with regular distribution of the air in the slurry by means of perforated horizontal tubes, is proposed. Some possibilities for cleaning of the orifices of the tubes are specially tested and it is found that by injecting water with the air every 30 minutes, the process can be carried out continuously without stopping for cleaning of the orifices. It is shown that at presence of catalysts, *Fe* and *Mn* ions, more than 99% of the slurry can be oxidized in 9 hours. The obtained after the drying of the slurry gypsum is white. The test of its compressive strength shows a value of 3.5 MPa, i.e. 40% higher than the requirements of the Bulgarian national standard for building gypsum. The obtained data are used for designing the oxidizer of an industrial installation for purification of flue gases from SO_2.

ACKNOWLEDGEMENTS:

This work is funded by the National Science Fund at the Bulgarian Ministry of Education, Science and Youth, contract No DO02, 361/30.12.2008.

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