

IRENA TRZEPIERCZYŃSKA*, MIECZYSLAW ADAM GOSTOMCZYK*

SCALING AND PLUGGING PROBLEMS IN WET FGD METHODS

On the basis of literature reports, the scaling and plugging problem encountered during flue gas desulfurization by the lime/limestone method is discussed. Desulfurization by the dual alkali method (where use is made of calcium compounds for the regeneration of the scrubbing liquor) fails to eliminate scaling or plugging. In the experimental part, the scaling and plugging problems are examined in an industrial FGD system (in two thermal power stations) which involve a modified dual alkaline method. The deposit concentrating in the scrubber loop was found to be built predominantly of CaCO_3 (~70%) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (~25%).

1. INTRODUCTION

Lime/limestone scrubbing is still widely used in FGD systems to fix the sulfur dioxide which has been removed from the flue gas stream, particularly in power generation. In industry, most of the FGD methods involve wet processes [1], often modified by changing composition of the scrubbing liquor, or by rearranging the elements of the system in order to update the cost/benefit balance, the efficiency of absorption, the utilization of Ca^{2+} and the operating effectiveness of the FGD system as a whole.

SO_2 is fixed by aqueous solution of lime or limestone. The process can be described by a number of simple reactions, but the chemistry of the process that occurs in a three-phase system is sophisticated and still far from being fully understood. As a matter of fact, the understanding of the process chemistry is prerequisite to achieve an optimum absorption of SO_2 . However, much of the information reported in literature has been obtained on the empirical basis.

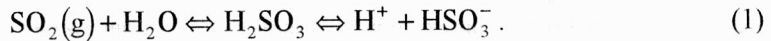
*Institute of Environment Protection Engineering, Technical University of Wrocław, Plac Grunwaldzki 9, 50-370 Wrocław, Poland.

The primary objective of this paper was to specify the scaling and plugging problems encountered in FGD systems which make use of wet lime/limestone methods. Another major objective was to assess the chemical and mineralogical composition of the deposit which forms in the scrubber loop of an industrial FGD system using the dual alkaline method.

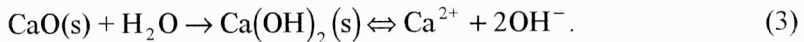
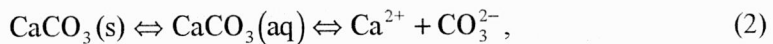
2. THEORETICAL BACKGROUND

2.1. PROCESS CHEMISTRY

The chemistry of the process involves the following reactions:
Absorption and dissociation of SO_2 :



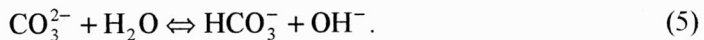
Dissociation of solid-phase components



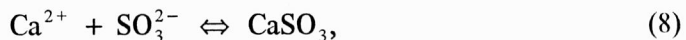
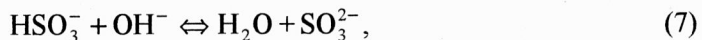
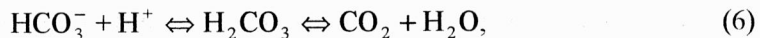
Dissociation of water



Hydrolysis



Other processes





The main aspects that can be brought under control by understanding the chemistry of the process are [2]:

absorption efficiency,

reagent utilization,

plugging and scaling,

quality of the waste products and potentiality for their utilization.

The operating parameters mentioned above are governed primarily by pH. The prerequisite of high SO₂ removal efficiency is a high pH level in the scrubbing liquor, because a low pH depresses the rate of SO₂ fixation. Excess H⁺ ions shift the equilibrium of the reaction (1) towards the left-hand side, thus leading to the desorption of SO₂. According to literature [2], SO₂ fixation in lime systems is the most effective when pH falls between 6.9 and 8.9. The limestone method, however, will not work when pH value is greater than 7.

The efficiency of SO₂ removal depends strongly on the reagent concentration on the scrubber loop, whereas the absorption rate is influenced by the rate at which the solid phase dissolves in the absorbing suspension.

The low solubility of the calcium compounds used in the lime system makes it necessary to build up a high absorbent-to-SO₂ ratio which, in turn, accounts for a low degree of reagent utilization (figure 1). To improve the latter it is necessary to decrease the pH level and to increase the solubility of the solid species. Solubility can be upgraded by modifying the composition of the scrubbing liquor. Thus, adding a cation which in the reaction with basic anion (CO₃²⁻, SO₃²⁻) is ready to form more freely soluble species than calcium salts – we can change the equilibrium of the lime system. Of various cations, magnesium ions were found to be best suited for this purpose [3]. Producing compounds (MgSO₃, MgSO₄) which are many times as soluble as the correspondent calcium salts, magnesium increases the concentration of available basic species (responsible for the absorption of SO₂), raises removal efficiency, and reduces precipitation of practically undissolved calcium compounds. Magnesium sulfite was found to be about 300 times as soluble as calcium sulfite, thus its small amount (~5%) was sufficient to obtain removal efficiency desired.

Lime/limestone scrubbing has a number of drawbacks, of which the concentration of undissolved reactant in the absorber loop, as well as hard scale build-up and plugging in the equipment are particularly troublesome. Scaling and plugging are very complex phenomena which depend not only on the design parameters, but also on the variables and chemistry of the process. Needless to say that it is one of the main reasons for erosion, increased energy demand (due to the pressure drop in the absorber [4]) and shut-downs.

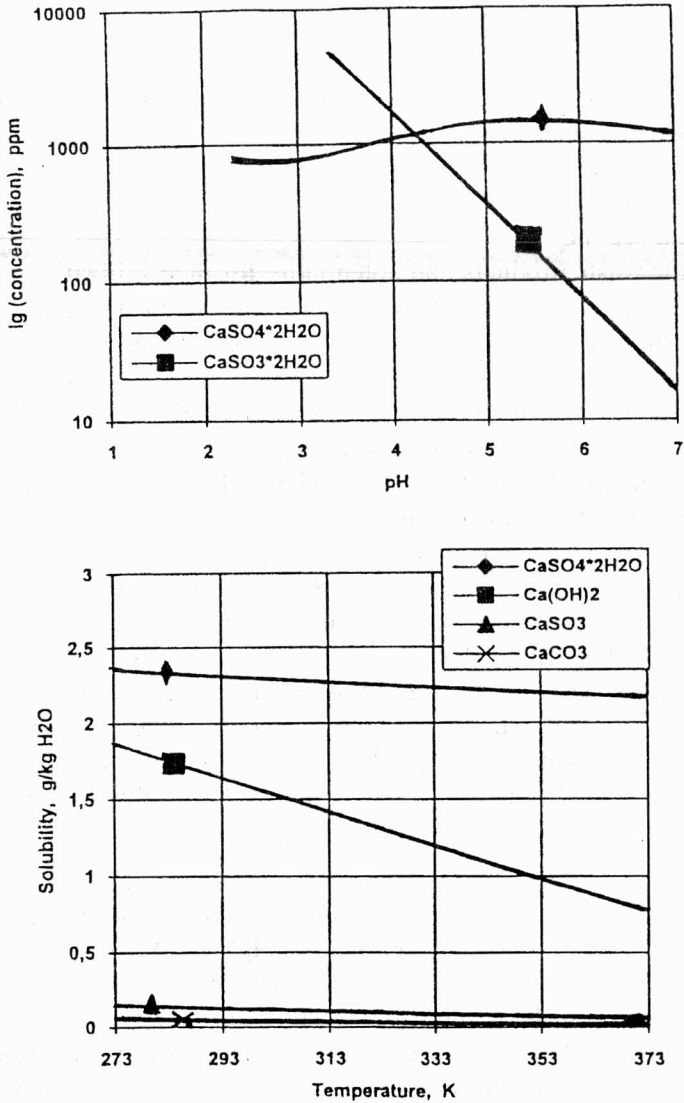


Figure 1

2. CONCENTRATION OF UNDISSOLVED SOLIDS IN THE ABSORBER LOOP

The lime/limestone method produces three types of scaling: sulfite scaling in the form of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$, sulfate scaling in the form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and carbonate scaling. It has been proved experimentally that precipitation of calcium sulfite and cal-

cium carbonate can be brought under control to a great extent by keeping the pH level below 9. In engineering sulfite scaling rarely takes place in limestone scrubbing, because the pH level required for this method must fall below 7. The phenomenon of scale build-up due to calcium compound precipitation occurs when the scrubbing liquor supersaturates. When the nucleation sites appear at that moment, crystallization will set on.

To measure the degree of supersaturation, use is made of the ratio of the ion activity product to the solubility product, which takes the following form

$$\frac{a_{\text{Ca}^{2+}} a_{\text{SO}_3^{2-}}}{K_{a_{\text{CaSO}_3}}} \quad \text{or} \quad \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}}{K_{a_{\text{CaSO}_4}}} \quad (10)$$

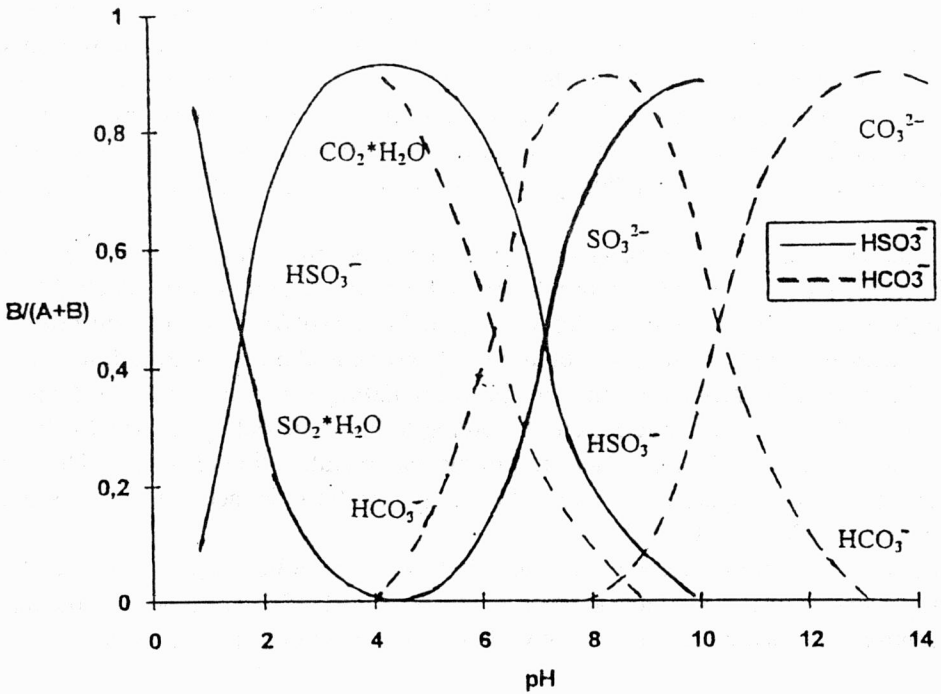


Figure 2

Experiments have shown that the risk of deposition occurs at a factor of 1.5 and 7 for calcium sulfate and calcium sulfite, respectively [3]. In the limestone system, the pH level in the scrubbing liquor ranges between 4 and 6, and that is why acidic calcium sulfite becomes dominant (figure 2). If there is a rapid local pH rise in the scrubber, in the pipes or in the holding tank, there will also be a concomitant precipitation of CaSO_3 . The application of the

limestone method is advantageous because the $\text{CO}_3^{2-}/\text{HCO}_3^-$ system exerts a buffering effect, thus adjusting the pH level between 5 and 6, which prevents precipitation.

Sulfate scaling is more difficult to control. Unlike calcium sulfite, the pH drop in the scrubbing liquor does not help to hold calcium sulfate in solution, because the solubility of these species increases only slightly with the increasing pH (figure 1). The amount of calcium sulfate rises when the content of calcium sulfite (which oxidizes at a rate dependent on O_2 contained in the flue gas stream, on fly ash concentration and pH [6]) is high. The rate at which calcium sulfite oxidizes increases with the decreasing pH, so it is unreasonable to believe that sulfate scaling will be prevented by appropriate pH adjustment.

The proneness of CaSO_4 to deposition is concomitant with its tendency to supersaturation. Deposition at supersaturation can occur via nucleation or crystal growth which sets on in the scrubber interior where many crystallization sites are found. Thus, the concentration of calcium sulfate should fall below the saturation level (which approaches 1.4) to protect the system against spurious deposition. The saturation of calcium sulfate depends primarily on the composition of the solid phase in the scrubbing solution. Under favourable conditions in the scrubber, oxidation of calcium sulfite does not exceed 20%, so there exists coprecipitation of sulfate and sulfite in the form of mixed crystals, which automatically reduces supersaturation with respect to calcium sulfate.

Another method of decreasing supersaturation (and preventing formation of sulfate scale) is the recirculation of gypsum. It should be noted that an approximately 5% concentration of solid gypsum in the slurry was found to be sufficient for this purpose. One of the methods which are used to obtain the 5% concentration required is forced oxidation. Addition of gypsum crystals into the recirculating slurry may also be helpful in providing sites for sulfate nucleation. According to literature data [2], a total solid content ranging between 10 and 15% is best to induce crystallization of sulfate. The degree of saturation with respect to calcium sulfate may also be influenced by the presence of other ions, e.g. Mg^{2+} or Cl^- [6].

Summing up, precipitation of calcium sulfate in the absorber loop is influenced by so many factors that it is impossible to identify precisely which of them might be important for the control and, consequently, for the prevention of this undesirable phenomenon.

3. EXPERIMENTAL

3.1. DESCRIPTION OF THE FGD METHOD

The staff of the FGD research group, Institute of Environment Protection Engineering, Technical University of Wrocław, Poland, modified the well-known dual alkali method (referred to as DAM) [7]. In the DAM, the FGD process is run in a special scrubber which provides heating of the flue gas stream and regeneration of the scrub-

bing liquor at the same time. The treatment of the flue gas with an alkali solution yields simultaneous removal of particulates and sulfur dioxide. The effluent from the sorption process is regenerated continually with whitewash. The final product includes predominantly the following species: hydrated calcium sulfate, dust particulates, calcium carbonate and non-converted calcium hydroxide. Commercial-scale FGD systems of that type have been operated in two municipal thermal-electric power stations to desulfurize the flue gases from two WR-25 boilers at each of two plants.

3.2. ANALYSIS OF THE PLUGGING DEPOSIT

The samples of the deposit which concentrates on the scrubber loop in the front of the nozzles which pass the liquor to the scrubber were analyzed. Samples were collected on the third day after pipe replacement. The scrubbing liquor was recirculated in a closed loop for five months.

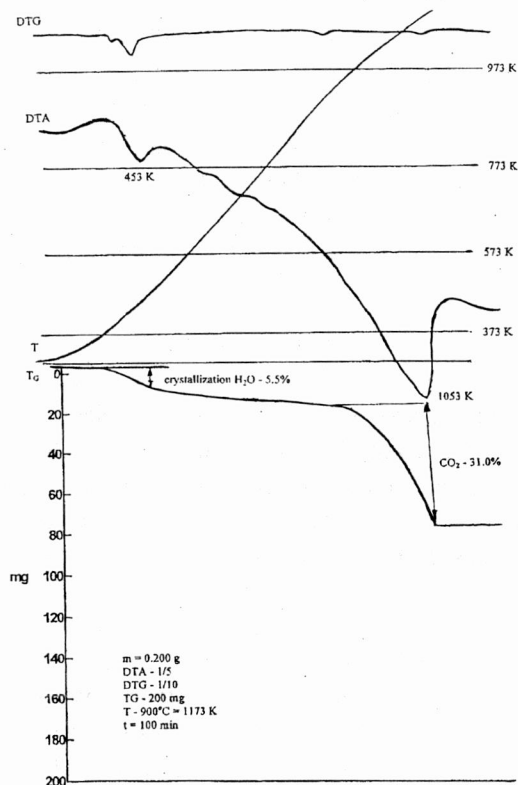


Figure 3

The parameters of the scrubbing liquor can be itemized as follows: pH, temperature and pressure varied from 10 to 11, from 301 to 305 K, and from 354 to 405 kPa, re-

spectively, whereas ion content averaged 0.554, 0.051, 1.185 and 1.80 kg/m³ for Na⁺, K⁺, Ca²⁺ and SO₄²⁻, respectively.

The deposit was subject to thermal analysis in the temperature range of 293–1173 K (figure 3), at weighed amounts of 200 mg and a TG sensitivity of 200 mg (DTA and DTG amounting to 1/5 and 1/10, respectively).

The results of chemical analysis were compared with those obtained by derivatography.

3.2.1. RESULTS OF PHYSICO-CHEMICAL AND THERMAL ANALYSES

Losses due to calcination were 2.8, 7.5 and 39.5% at 378, 513 and 1173 K, respectively, whereas Ca, Na, Mg and SO₄²⁻ contents amounted to 32.90, 0.35, 0.04 and 14.17 dry wt.%, respectively.

Thermal analysis of the deposit (dried at 323 K) revealed a total weight loss of 40.5%. The loss of CO₂ amounted to 30.5%. Total H₂O loss equalled 6.5% (water of crystallization and hygroscopic water accounting for 5.25 and 1.25%, respectively). On the basis of these data, CO₂-bound calcium, calcium carbonate, SO₄²⁻-bound calcium, Ca-bound sulfate ion and CaSO₄·2H₂O were calculated, amounting to 27.73, 69.32, 5.83, 14.00 and 25.08%, respectively. $\Sigma(\text{CaCO}_3 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}) = 94.4\%$.

Thermal analysis revealed no detectable occurrence of phases other than dihydrated calcium sulfate (25.1%) and calcium carbonate (69.3%).

The results of all the analyses performed are similar, so it can be anticipated that the composition of the depositing solids has been determined correctly.

4. DISCUSSION

We have learned from our experience that carbonate scaling and sulfite scaling can be efficiently controlled by keeping the pH well below 9 [2]. Scaling and plugging phenomena seldom occur (if at all) in the limestone scrubbing because it is run at pH ~ 5.5. The limestone method, however, applies only to the FGD systems operating in large power plants, and becomes useless when applied to FGD in small industrial objects or municipal thermal-power stations. No wonder that the latter prefers lime scrubbing, which implies that carbonate scaling is no longer negligible.

In wet FGD processes, the scrubbing liquor contains not only ions which are typical of the absorption of sulfur dioxide, but also some other ions concomitant with the presence of, e.g., CO₂, HCl, O₂, NO_x, or HF in the flue gas stream.

Of these, CO₂ is a flue gas component competitive with SO₂. The two species differ between each other in solubility, which is indicated by the Henry constants ($H_{\text{SO}_2} = 0.03$, $H_{\text{CO}_2} = 1.2$) [7]. However, the partial pressures of the gaseous species carried by a typical flue gas (SO₂, 0.1–0.2 vol. %) are such that in the lime method the driving module for the absorption of CO₂ is greater than that for the absorption of SO₂.

The reactions in the $\text{CaO-SO}_2\text{-CO}_2\text{-H}_2\text{O}$ system have a similar course which was pH-dependent (figure 2). As shown by the plots in figure 2, $\text{SO}_2\text{-H}_2\text{O}$ and CO_3^{2-} contribute little to the stabilization of equilibrium in the pH range which is important for the absorption of SO_2 . When other ions are present in the scrubbing solution, the equilibrium is distribution of the ionic force to the solubility of both gaseous and solid species.

In industrial FGD systems, the effluents from the sorption process are in most instances recirculated after regeneration by calcium hydroxide treatment, as it is in the DAM method. The recirculating liquor becomes enriched with carbonates and sulfates (produced during absorption and oxidation, respectively) which are later removed in the course of the regeneration process.

According to the results of our study, the deposit accumulating in the pipes of the FGD system, which involves the DAM method, contains $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ (~25 wt.%) and CaCO_3 (~69 wt.%). Thus FGD by DAM method creates favourable conditions primarily for the precipitation of carbonates. According to the conditions of the absorption and oxidation processes, the pH and the composition of the scrubbing liquor stabilize to undergo changes in the course of the regeneration process. When slightly soluble species (Ca(OH)_2) is added to a system of salts which are in equilibrium, this equilibrium will be disturbed due to the influence of the 'common ion' and pH.

The equilibrium of slightly soluble salts in the saturated solution depends on their solubility product and on the pH of the solution. Thus:

$$[\text{Ca}^{2+}] = \frac{K_{r_1}}{[\text{OH}^-]^2}, \quad (11)$$

$$[\text{Ca}^{2+}] = \frac{K_{r_2}}{[\text{CO}_3^{2-}]}, \quad (12)$$

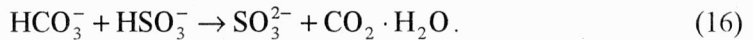
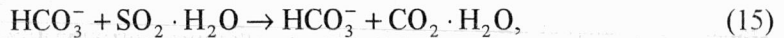
$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}, \quad (13)$$

$$[\text{CO}_3^{2-}] = \frac{K_{r_2}}{K_{r_1}} \times \frac{K_w^2}{[\text{H}^+]^2}. \quad (14)$$

The solubilities of the salts and their solubility products (K_r) are as follows:

CaCO_3	14 g/m ³ ,	$K_{r_2} = 4.7 \times 10^{-9}$,
Ca(OH)_2	1.52 kg/m ³ ,	$K_{r_1} = 5.5 \times 10^{-6}$,
$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	2.4 kg/m ³ ,	$K_r = 2.4 \times 10^{-5}$.

According to relation (14), the solubility of calcium carbonate is strongly pH-dependent. It follows that pH will be the best parameter to control the composition and equilibrium of the scrubbing liquor and, consequently, the scaling problem. Carbonate ions in the presence of sulfurous acid (which is stronger than carbonic acid) provide partial removal of carbon dioxide from the scrubbing liquor according to the following reactions:



The change of the pH level in the scrubbing liquor after regeneration brings about an immediate shift of equilibrium towards the formation of CO_3^{2-} ions and their precipitation in the form of CaCO_3 . The presence of the 'common ion', furthermore, raises the rate at which carbonates are precipitated [9]. Thus, it is impossible to prevent carbonate scaling in the absorber loop, particularly when the lime method is applied or when the regeneration process involves $\text{Ca}(\text{OH})_2$. However, it has been found that this type of scaling can be controlled to quite a large extent by keeping the pH at the level required.

5. SUMMARIZING COMMENTS

In the DAM method of FGD, the absorption of sulfur dioxide occurs at pH between 6 and 9. The conditions at which the FGD process is run make it possible to reduce corrosion, but they do not prevent scaling and plugging. The scaling and plugging phenomena are due to the hypersaturation of the scrubbing solution with respect to CaSO_4 and CaCO_3 which, in turn, results from the extended time of recirculation. It seems therefore advisable to remove temporarily excess salts from the scrubbing liquor (outside the scrubber loop) or to decrease the pH level (also outside the scrubber loop) for the removal of carbon dioxide.

Summing up, only a thoughtful intervention in the FGD technology can noticeably reduce scaling and plugging.

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PROBLEM ZARASTANIA INSTALACJI W WYNIKU STOSOWANIA MOKRYCH METOD ODSIARCZANIA SPALIN

Omówiono przyczyny i skutki zarastania aparatury i zatykania przewodów instalacji do mokrego odsiarczania spalin. Przedstawiono możliwości rozwiązania problemu, z którym spotykamy się szczególnie wtedy, gdy stosujemy metody wapienne. Na podstawie badań osadu z instalacji pracującej metodą DAM stwierdzono, że węglan wapnia stanowi ok. 70% osadu.

