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CURRENT PROBLEMS AND DEVELOPMENT IN FLUE GAS DESULFURIZATION

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Abstract

One of the most widely used processes of SO_2 removal from flue gases is absorption by slurry containing $CaCO_3$. The existing installations are designed for big capacity boilers and provide low degree of absorption. The stringent environmental protection regulations for SO_2 emissions in EU call for better solutions. The aim of the present discussion on the current problems and achievements in gas desulfurization is to help the finding of the proper direction of the efforts for developing of a new technology and the choice of apparatuses and equipment.

Key words: *wet flue gas desulfurization, SO_2 removal efficiency, bisulfite oxidation, lime, limestone, slurry, gypsum, scrubber.*

1. INTRODUCTION

The great problem of desulfurization of flue gases from combustion systems is solved, but only partially, for big steam generators with installation proposed by foreign companies. The achieved economically grounded percentage of SO_2 removal efficiency is about 95 % [1-3]. In Bulgaria the Consortium Klockner Industrie - Anlagen GmbH / S-H-U Saarberg Umwelttechnik GmbH in the period 1997 – 2002 realized a project "Desulfurization installation for 7th and 8th blocks of Thermal Power Station "Maritza Iztok 2". The experience is published in a report [4] showing that after a long term operation and enhancement the installation has reached its planned degree of absorption of 90%. Of all desulfurization technologies the most widely used are those with production of gypsum as a by-product and not because of economical advantages but because the gypsum can be used in great quantities as a building material or can be disposed as a waste product in lack of market. The height of the absorbers of this technology is over 20 m and even at relatively low degree of desulfurization from environment protection point of view. Classical packed bed columns which could decrease significantly the height of the absorption apparatuses are practically not used because of apprehension of packing fouling problems. The present work is a review of the main principles, technological solutions and recent study results on flue gas desulfurization (FGD) with an emphasis on wet limestone-gypsum technology, the most common FGD process. It is based on a report from 1978 [1], covering the period of the most rapid development of the investigations in that area, study results reported at a specialized Colloquium in 1983 [2] and resent research during the last 15 years.

FGD is the process of removing sulfur oxides, primarily SO_2, from combustion gases. The latter are contacted with an absorbent medium in either an absorber or a scrubber vessel [1]. The SO_2 is absorbed, neutralized and /or oxidized by the alkaline reagent into a solid compound, either calcium or sodium sulfate. The solid is removed from the waste gas stream using downstream equipment. Scrubbers are classifies as once-through (non- regenerable) or regenerable, based on how the solids generated by the process are handled [5]. Once-though systems either dispose the spent sorbent as a waste or utilize it as a byproduct. Regenerable systems recycle the sorbent back into the system. Both types of systems can be further categorized as wet, dry, or semi-dry: wet scrubbing using a slurry of

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sorbent, usually limestone or lime, to scrub the gases; semi-dry scrubbing (spray dryers) using similar sorbent slurries and dry systems, injecting pneumatically powdered sorbent. There are approximately about 20 different kinds of SO_2 removal techniques available [6]. In 2000 there were about 680 FGD systems installed in 27 countries worldwide and 140 were under construction or planned in 9 countries [7]. According to the statistics data published in [5] FGD scrubbers have been applied to combustion units firing coal and oil that range in size from 5 MW to 1500 MW. Dry scrubbers and spray scrubbers have generally been applied to units smaller than 300 MW. Approximately 85% of the FGD units installed in the US are wet scrubbers, 12% are spray dry systems and 3% are dry injection systems. The highest SO_2 removal efficiencies (greater than 90%) are achieved by wet scrubbers. The capital, operating and maintenance costs per short ton (907.18474 kg) of SO_2 removed (in 2001 US dollars) are: for wet scrubbers larger than 400 MW, the cost is $200 to $500 per ton; for wet scrubbers smaller than 400 MW, the cost is $500 to $5 000 per ton, for spray dry scrubbers larger than 200 MW, the cost is $150 to $300 per ton, for spray dry scrubbers smaller than 200 MW, the cost is $500 to $4 000 per ton.

2. WET FLUE GAS DESULFURIZATION SYSTEMS

In a wet system, flue gas is ducted to a spray tower where an aqueous slurry of sorbent, typically limestone or lime, is injected into the flue gas [5]. SO_2 dissolves into the slurry droplets where it reacts with the alkaline particulates. The absorber effluent is sent to a reaction tank where SO_2- alkali reaction is completed forming neutral salt. In limestone forced oxidation air is added to the reaction tank which oxidizes the spent slurry to gypsum [5]. The gypsum is removed prior to the slurry being recycled to the absorber.

2.1. Lime slurry flue gas desulfurization systems

Lime slurry scrubbing is a wet scrubbing process that uses lime slurry to remove SO_2 from flue gas [1]. Dry calcium oxide (CaO) is fed to the system and reacted with water to form a slurry. This slurry is contacted with the flue gas and absorbs SO_2. The SO_2 reacts with the slurry to form calcium sulfite, which is removed from the system as a sludge. The flue gas flows from the boiler into electrostatic precipitator's, where 99 percent of the particulate is removed. The flue gas then flows through an induced draft fan into the absorber module. Lime is fed from a feed bin to a slaker, where it is slurried with fresh water, diluted with recycled water and fed into the reaction tank. A bleed stream from the recirculating slurry goes to a thickener, the underflow from which is pumped to the sludge pond. Pond water and overflow from the thickener are returned to the system. Makeup water enters as mist eliminator wash and as fresh water feed to the slaker. Clean gas from the scrubber absorber is reheated, using heated air, and discharged to the stack. From the process material balance it is seen that at coal sulfur content of 3.5% the SO_2 removal efficiency in these installations is 90%. The sludge oxidation $CaSO_3/CaSO_4$ ratio is 90:10. The liquid to gas (L/G) ratio in the absorber is 5.3 l/m^3. The SO_2 removal efficiency of the FGD system at Green River Power Station is even lower only 80%. In the Mohave Test Plant at coal sulfur content of 0.8% the SO_2 removal efficiency is 95%, increasing significantly with increasing of the L/G ratio. At initial sulfur concentration of 200 ppm, the SO_2 removal efficiency reaches 80%. The theoretical effect of L/G ratio on SO_2 removal efficiency is shown in Fig. 1 for a spray tower predicted by a mathematical model for the Shawnee plant, based on test data. It is seen that at the same other conditions the SO_2 removal efficiency at pH 6 is 70% and at pH 9- about 92%.

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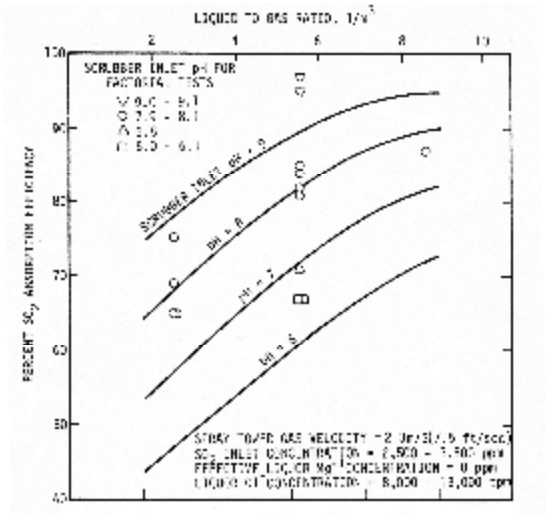


Fig. 1. Liquid to gas ratio and scrubber inlet pH versus predicted and measured SO_2 removal, spray tower with lime slurry, Shawnee plant, [1, Fig. 3-15]

2.2. Limestone slurry flue gas desulfurization systems

According to the limestone slurry method calcium hydroxide is replaced by finely ground calcium carbonate (limestone). Since the sulfurous acid obtained in SO_2 dissolving is many times stronger than the carbonic acid, the calcium carbonate turns into calcium bisulfite and calcium sulfite. Like in the lime slurry method by the oxygen of the flue gases and especially by air fed in the system it turns into $CaSO_4$ $2H_2O$ which is transformed by drying to gypsum ($CaSO_4.0,5H_2O$) for building material. The first system of this type in USA started operation in 1965. Part of the ground limestone is passed into the boiler and the rest in the absorption unit for additional reduction of the SO_2 concentration in flue gas. The presented data for 12 installations built in the period 1965-1977 shows that the degree of decreasing of SO_2 emissions varies from 50 to 92%. Fig. 2 [1] presents a flow diagram of the installation built at one of the boilers of La Gygne No 1 Power Station. The flue gas after the air heater enters the Venturi scrubber, it is subjected to jets of limestone slurry injected through nozzles on the walls of the vessel. The liquid-gas stream flows downward through the Venturi throat restriction, where the gas contacts the atomized liquid droplets. As the gas leaves the Venturi and enters the disengagement chamber, its velocity decreases. This reduction in velocity separates the limestone slurry droplets from the quenched gas. The slurry drains into the recirculation tank. Gas enters the SO_2 absorption tower at the base and moves upward through two sieve trays in series. As the gas passes through the 34.9-mm-diameter holes of the sieve trays, it contacts a shower of limestone slurry, which is sprayed into the path of the rising gas. The scrubbed gas then passes through a third sieve tray, which collects slurry carryover and reduces the load on the demister. The gas then passes through a chevron demister, where the remaining fine droplets are collected. The flue gas is then heated before it enters a plenum common to all modules and is discharged to the stack through induced-draft fans. The Venturi and the absorber tower of each module share a common limestone slurry recirculation tank, in which the pH is maintained between 5.5 and 6.0. The pH is monitored by means of a cell located in the slurry feed to the Venturi nozzles. A hydrocyclone has been installed in the slurry circuit of each module to remove large particles. The liquid level in the recirculation tank is maintained by pumping excess liquor to the sludge disposal pond. The SO_2 removal efficiency of the unit varies from 76-83%.

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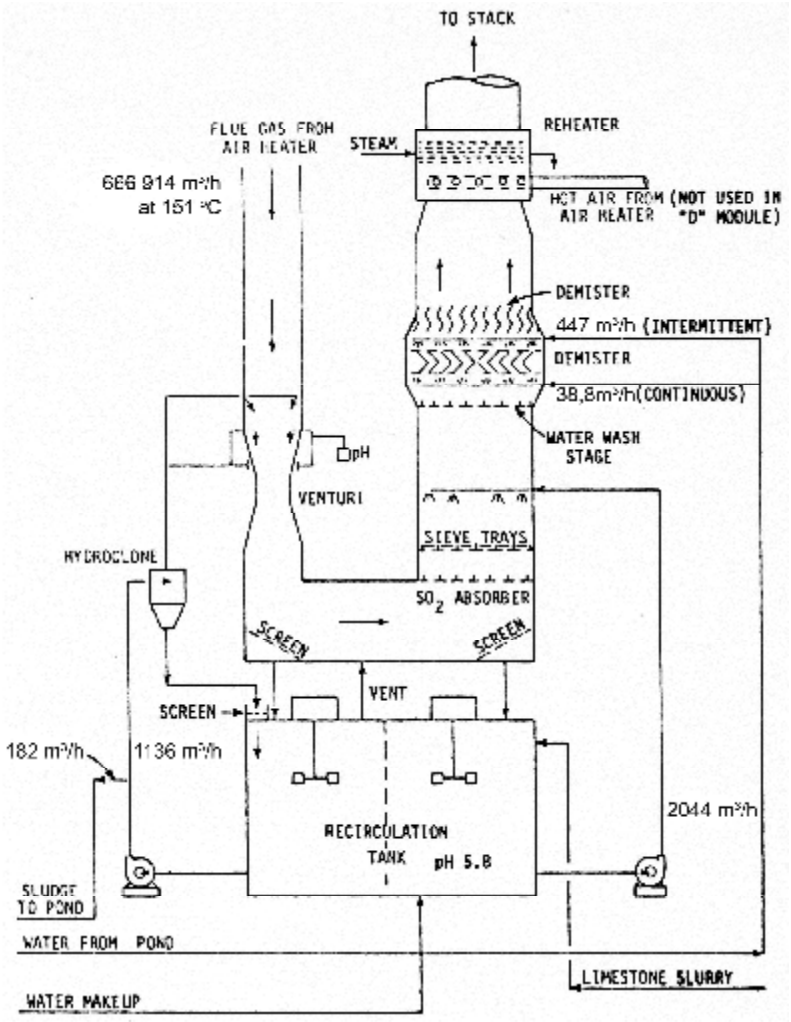


Fig.2. Flow diagram of one of the 8 FGD modules- La Gygne No 1, [1, Fig. 3-27].

The presented data for 17 Japanese installations of this type show that their SO_2 removal efficiency varies from 84 to 99%. In all cases the initial SO_2 concentration in the flue gas is low from 0.04 to 0.16 %. In Fig. 3 data is presented for the influence of the L/G ratio at different values of pH on the SO_2 removal efficiency in the Shawnee Plant operating with the same technology. It is seen in Fig. 3 that the pH reduction leads to significant reduction of SO_2 removal efficiency. Some other results for the same system are presented in Fig. 4. In the same plant the influence of the Mg^{++} ion concentration on the SO_2 removal efficiency with limestone slurry is studied. The results are presented in Fig. 5. The favorable influence of the Mg^{++} ion concentration on the absorption efficiency is due to the increased solubility of the respective magnesium salts which act as carriers of the SO_2 to the limestone particles.

2.3. Double alkali flue gas desulfurization systems

Double alkali technique involves absorption of SO_2 by an alkaline solution, generally sodium salt solution, in the scrubbing device and treatment of the scrubber effluent with lime or limestone in a separate reactor outside the scrubber loop. Calcium sulfites and sulfates are precipitated and discarded, whereas the scrubbing liquor is regenerated and returned to the loop. The process can achieve very

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high SO_2 removal efficiency, but because of complexity it is inapplicable to middle and small capacity plants.

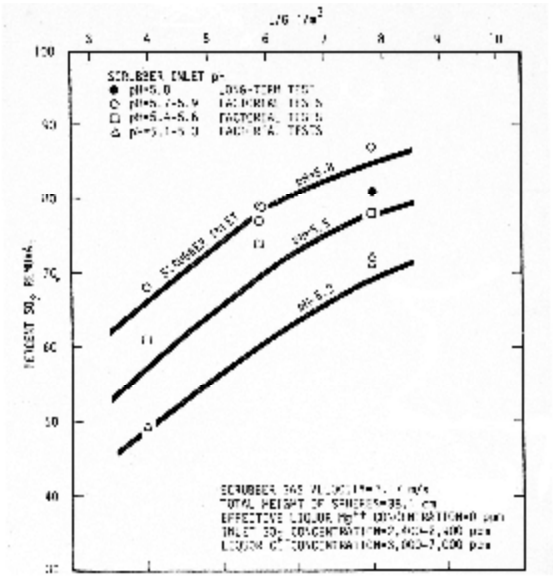


Fig. 3. Liquid to gas ratio and scrubber inlet pH versus predicted and measured SO_2 removal- spray tower with limestone - Shawnee plant [1, Fig. 3-30]

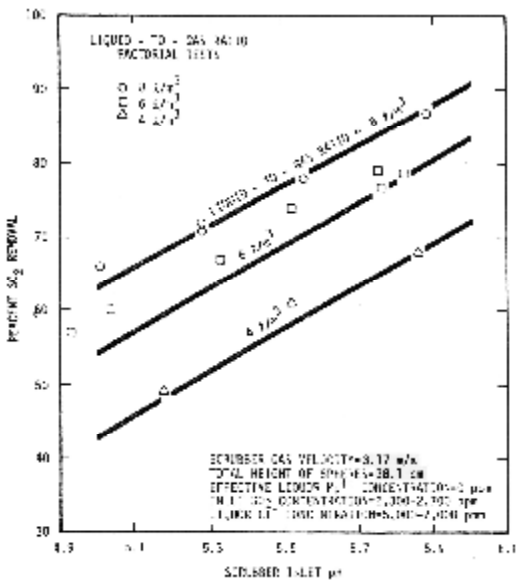


Fig. 4. Influence of scrubber inlet pH on SO_2 removal efficiency at various liquid to gas ratios, spray tower with limestone- Shawnee plant [1, Fig. 3-32]

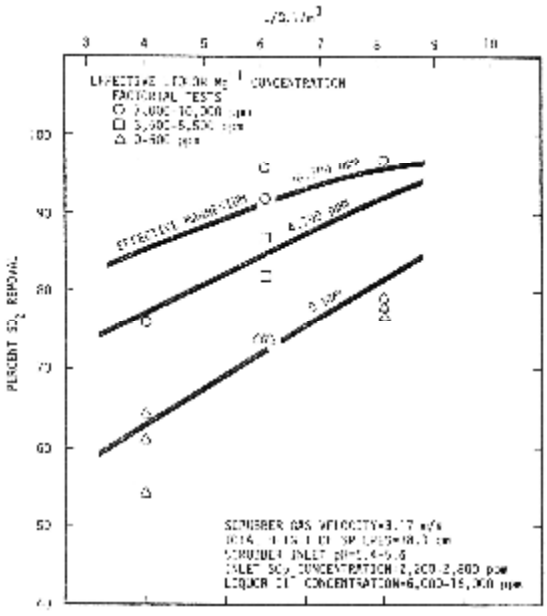


Fig.5. Influence of liquid to gas ratio on SO_2 removal efficiency at various magnesium ion concentrations, spray tower with limestone- Shawnee plant [1, Fig. 3-33]

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3. METTHODS OF WET FLUE GAS DESULFURIZATION

In the materials of a Colloquium [2] held in 1983 advanced for that time methods and absorbers for removal of SO_2, NOx and dust from flue gases were described and commented.

3.1. Saarberg-Hölter-Lurgi method

One of the first installations of FGD in Germany was realized by the Consortium Saarberg [2, p. 89] employing the method of Saarberg- Hölter- Lurgi. It uses lime slurry as an absorbent. A substantial characteristic of the method is addition of small quantities of organic acid in the slurry, 0.5-1 g/l. The presence of the acid leads to slurry buffering and maintaining of constant pH.

3.2. Bischoff method

The FGD with obtaining of gypsum by the Bischoff method is described in [2, p.73-76]. In principle the absorption process with obtaining of calcium sulfite from calcium carbonate and SO_2 is similar to the commented above. The oxidation occurs in an acidic medium by the oxygen of the air. Acidifying by sulfuric acid is necessary for the transforming of the sulfite into soluble bisulfite, with the aim to conduct the oxidation in the liquid phase and to avoid the process control by the oxygen transfer from the liquid phase to the solid calcium sulfite. The oxidation process occurs in a separate oxidation zone of the reactor with bubbling air. At the same time it takes away also the CO_2 formed by the reaction of calcium carbonate, not reacted in the absorber, with the sulfuric acid or with the calcium bisulfate.

3.3. Two stage absorption method

Results of the industrial operation of a FGD system of the Consortium KRC/EVT, are commented in [2, p. 77-82]. The applied method is two-stage absorption with a limestone slurry. The flow diagram is presented in Fig. 6, [2, p. 77]. The scheme of the absorber is shown in Fig. 7 [2, p.78]. The oxidation zone is situated at the absorber bottom in which air is passed by a compensation unit. From bottom to top the following elements follow: the flue gas inlet, two rows of nozzles feeding slurry coming from the hydrocyclone, Fig. 6, collector for passing the partially treated slurry to the absorbent tank, two rows of nozzles feeding slurry from the absorbent tank, one raw of nozzles distributing slurry over a film absorption packing and two successive rows of droplets capturing packing washed from below by process water through nozzles. The advantage of the two-stage absorption, especially with variable regime of SO_2 concentration in the flue gases, is the possibility in the second stage down the gas stream to maintain a great excess of limestone, practically with no excess for the process as a whole. Thus in the second stage pH is kept in the range 6-7. The shortcoming is that at this pH calcium sulfite coats the calcium carbonate particles, which impedes the contact of the sulfurous acid with the calcium carbonate inside. This shortcoming is overcome in the first stage down the gas stream, where because of the increased SO_2 concentration, the slurry pH drops and the calcium sulfite is dissolved to bisulfite. By the oxygen of the fed air the bisulfite is oxidized to bisulfate from which calcium sulfate bihydrate is deposed and leaves the system as gypsum. After drying and partial dehydration to hemihydrate, it is used for building material. The absorption degree of these systems varies from 92 to 98% dependent on the conditions. In Fig. 8, [2, p. 83] a scheme of the absorber of the Steinmüller Company is shown. The gas enters the apparatus from the top through an inlet coaxial duct and passes into Venturi throat restrictions. Just before that it is subject to jets of limestone slurry. Due to the strong turbulence in the restrictions the droplets are pulverized and the absorption rate is high. The gas flow turns contrariwise through a ring duct in countercurrent to the slurry fed by nozzles. Upwards droplets capturing zone follows subjected to water jets and the purified gas leaves the apparatus.

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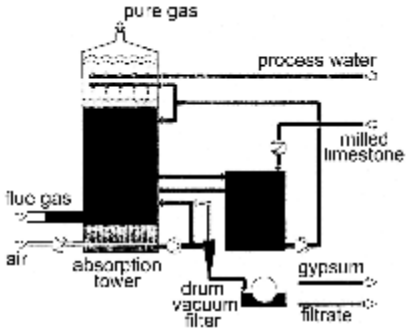


Fig.6. Flow diagram of the KRC method. [2, p. 77].

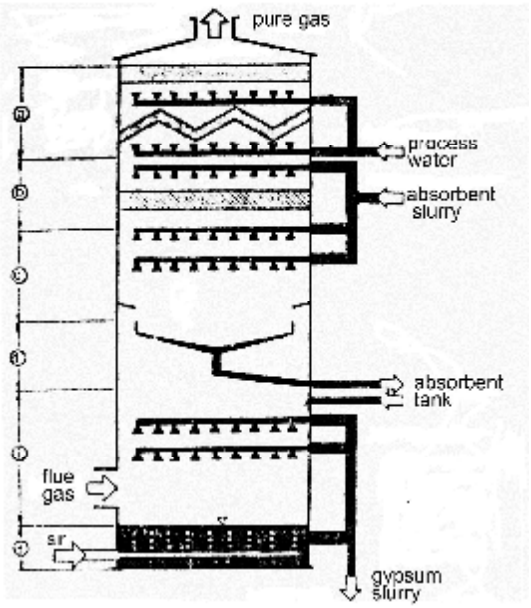


Fig. 7. Absorption tower [2, p. 78]
a- droplets catching zone; b- film absorption packing; c- spray zone; d- collector; i- spray zone; f- oxidation zone.

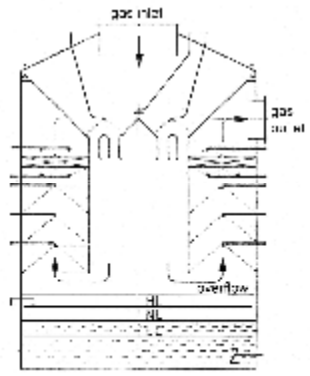


Fig. 8. Two-stage Ventury absorber, Steinmüller, [2, p. 83.]
HL-maximal level; NL-operation level; LL-minimal level.

The second construction shown schematically in Fig. 9, [2, Fig.7, p.85], is characterized by low pressure drop. The capacity of this apparatus reaches 2 million m^3/h. The flow diagram is presented in Fig. 10, [2, Fig. 14, p. 78]. It is shown that the integration of the oxidation zone into the apparatus does not lead to reduction of the degree of absorption and limestone utilization.

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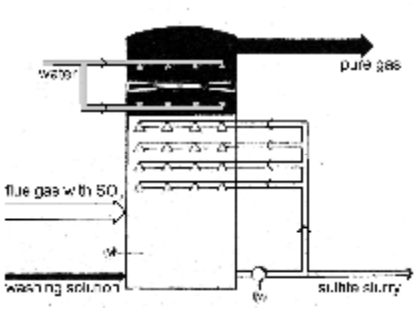


Fig. 9. Two-stage absorber, Steinmüller [2, Fig. 7, p.85]

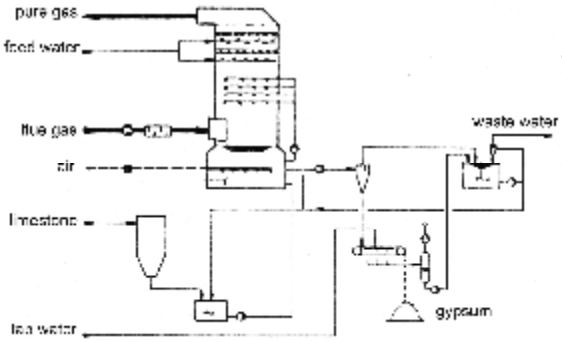


Fig. 10. Two-stage absorption flow diagram, Steinmüller, [2, Fig. 14, p.87]

The desulfurization system of the Heilbronn Power Station is similar to that shown above. The absorption is conducted at a temperature of 45-46°C. Fig. 11, [2, Fig. 3, p. 95], is a scheme of its unit for drying of calcium sulfate bihydrate to gypsum, calcium sulfate hemihydrate, for building material.

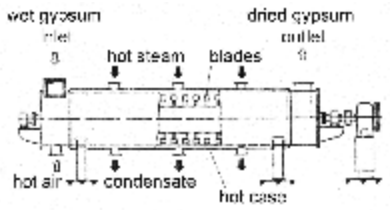


Fig.11. Unit for drying of calcium sulfate bihydrate to gypsum, Heilbronn Power Station, [2, Fig. 3, p. 95]

4. KEY PROBLEMS OF THE STUDIES ON WET FLUE GAS DESULFURIZATION IN THE LAST 15 YEARS

An overview of wet FGD systems Fig. 12 and dry FGD systems using limestone as an absorbent is presented in [8].

Oxidation tower-separated type

In-absorption tower oxidation type



Fig. 12. Limestone-gypsum process-based desulfurizers, [8]

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4.1. Bulgarian experience in wet flue gas desulfurization (WFGD)

In order to answer the European regulations for Environment protection and to optimize the equipment operation Maritzha Iztok 2 Power Plant 1450 MW has started large projects for building of FGD systems and rehabilitation of the plant blocks. The aim is to reduce the harmful emissions of the flue gases and dust concentration, to decrease the SO_2 emissions with 94% and to increase the power production with 156 MW [9]. Large scale tests are performed [4] in the FGD system of 7th and 8th blocks of Maritzha Iztok 2 Pawer Plant, burning lignite coal with sulfur content from 2.5-6%. The system is of wet limestone type with forced oxidation, Fig. 13. Its cost is 110 million DM. The main contractor is the German Consortium Klockner INA/SHU. For operation of the FGD system of 7th and 8th block of 6500 h/year the average reduction of the emissions of SO_2 is 200 000 t. Besides the SO_2 the system removes from the gases also HCl and HF. The flow chart and the basic units are similar to those shown in Fig. 13 with additional feeding of air at the mixers of the settler. The limestone for the slurry with particle size 0-10 mm is subjected to wet milling. The slurry passes into hydrocyclones for separation. The upper slurry stream is fed in the limestone slurry tanks. The slurry characteristics there are the following: solid phase content 25%, particle size $R_{63} \leq 10$. The so prepared slurry is passed to the absorber by pumps. The flue gas after the boiler enters the absorber above the free liquid surface and flows upward through the apparatus. The slurry consisting mainly of water, gypsum and limestone is pumped from the bottom of the absorber to its upper part and is sprayed by a system of nozzles in a countercurrent to the gas. The water absorbs SO_2, HCl и HF. At the next stage the limestone and the oxygen react with the dissolved gases to produce gypsum, calcium chloride and calcium fluoride. The oxygen is fed in the absorber by the compressor for oxidizing air directly into the settler.

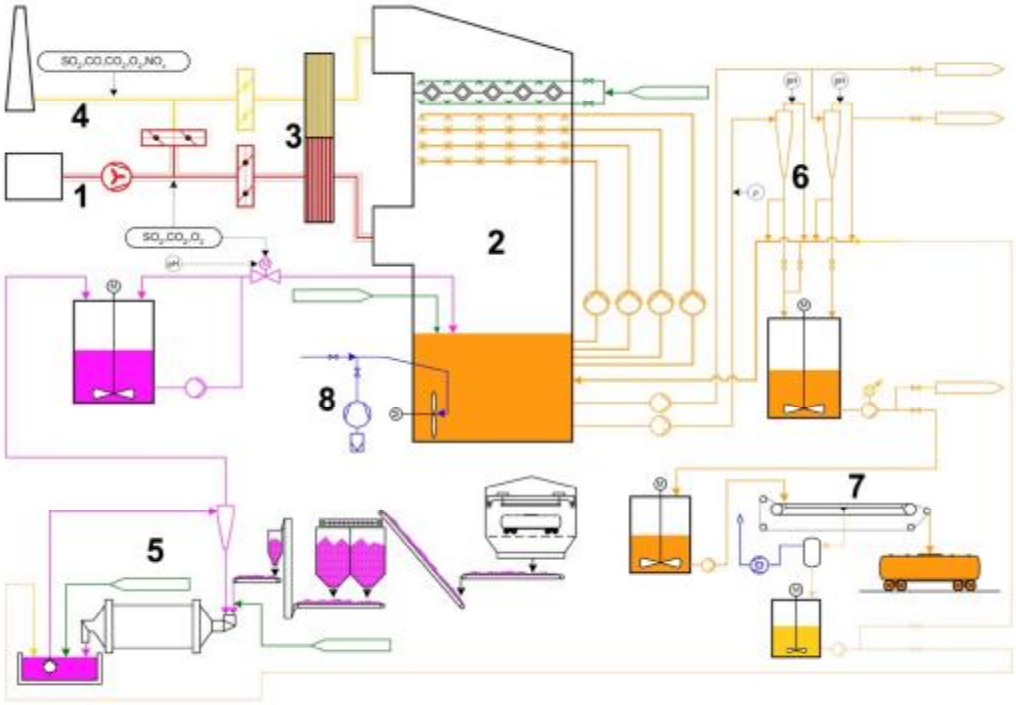


Fig. 13. WFGD system of 7th and 8th blocks of Maritzha Iztok 2 Power Plant, [4]
1- Untreated flue gas inlet; 2- Flue gas cleaning, 3- Reheating of treated flue gas, 4- Treated flue gas outlet, 5- Limestone milling, 6- Gypsum slurry separation, 7- Gypsum dewatering, 8- Oxidation air.

There the obtained gypsum crystals grow bigger. The big particles gypsum is separated in a system of slurry pumps and hydrocyclones. The slurry of the upper stream goes back into the absorber and the dense consisting big particles gypsum slurry is passed according to the needs to excavator pump station or to the band vacuum filters of the dewatering system. The gypsum containing 10 % free moisture is stored by band conveyor in a depot for dry gypsum from where it can be transported by train or trucks. The filtrate goes back into the limestone slurry system or into the absorber. It has been noted that the degree of the dissociation reaction

$SO_2(aq) + H_2O \leftrightarrow HSO_3^- + H^+$

increases with increasing of pH from 0 to 4.5 leading to a reduction of the concentration of the dissolved not dissociated SO_2 and to an increase of the bisulfite ions concentration in the liquid. For pH over 4.5 the bisulfite ions start dissociating to sulfite

$HSO^- \leftrightarrow SO^- + H^+$.

In increasing pH over 5.5 the sulfite ions concentration increases significantly at the expense of the bisulfite ions. The obtaining of sulfite ions is unwanted because in the reaction of $CaCO_3$ of the limestone calcium sulfite is obtained which covers the limestone particles and leads to blocking effect as a result of which the calcium carbonate stops to react.

4.2. Optimization of WFGD processes by computer simulation

A Computational Fluid Dynamics (CFD) model for a flue gas desulfurization plant of the wet scrubber type, and its application to an operating plant is presented in [3]. The sorbent used is limestone, and, after cleaning the flue gases, the limestone slurry is collected in an oxidation tank for the production of gypsum. The essential mass-transfer mechanisms are accounted for, as are also the main chemical kinetics leading to the formation of gypsum. The model is applied to the FGD plant of the Teruel Power Station located in Andorra (Teruel, Spain), fired with a high-sulfur coal (up to 4,5 percent), and the FGD system has been designed for a desulfurization capacity of 1.4 million Nm^3/h for a desulfurization efficiency better than 90 %. Validation of the model is conducted by comparison with available plant data for two levels of sulfur contents in the coal (3.5 and 4.5 percent) and two desulfurization efficiencies (50 and 95 %). The absorber consists of a cocurrent and a counter-current tower (Fig. 14). The flue gas enters the device through the cocurrent section, where it is showered with the limestone slurry injected through the limestone nozzles. While flue gases and slurry flow in this cocurrent section, SO_2 from the gas is partially absorbed into the slurry. At the bottom of the absorber there is a slurry oxidation and neutralization tank. The cocurrent slurry droplets disengage from the gas flow and fall to the tank, while the gases turn 180^o towards the counter-flow section of the absorber, where it is further sprayed with limestone slurry. In the counter-current stream, a grid enhances the contact between gas and slurry. The counter-current slurry falls into the tank, while the flue gas leaves the FGD plant after passing through two arrays of mist eliminators. Thus, in the absorber the slurry pH decreases as SO_2 is absorbed, and in the tank it increases due to the dissolution of limestone and the CO_2 desorption. The range of values agrees well with plant observations, which indicate that pH in the tank is between 5.2 and 5.6. The isosurfaces of SO_2 concentration in Fig. 15 show that the cocurrent section of the absorber accounts for most of the SO_2 removal; and also in all cases the influence of the residence time on the SO_2-concentration pattern in the countercurrent section is apparent. For the calculated desulfurization efficiency it is commented that while other similar plants attain this degree of desulfurization efficiency with the addition of organic acids, this plant relies on greater slurry-gas ratios, lower flue gas velocities and finer limestone-particle size.

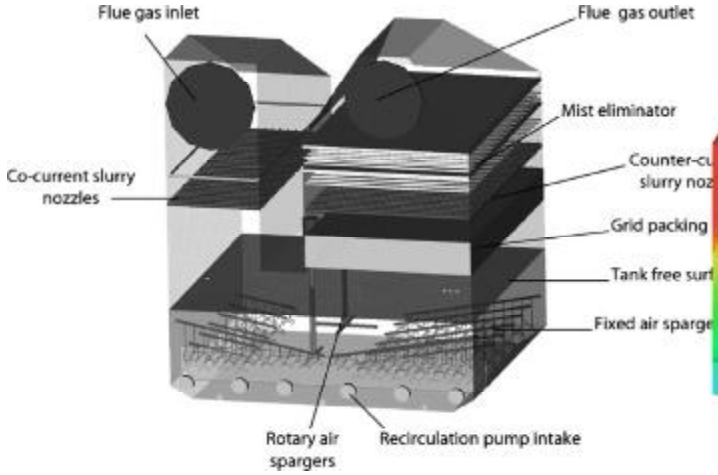


Fig. 14. Schematic of the FGD plant, [3].

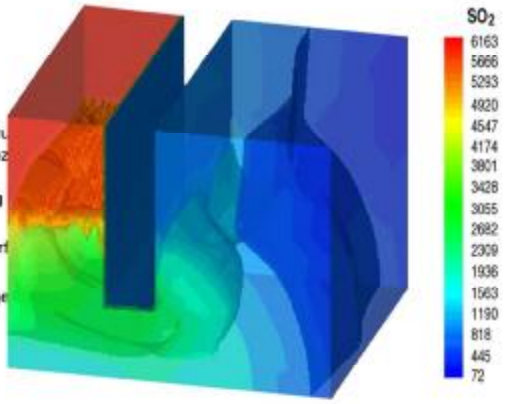


Fig. 15. Contours of SO_2 concentration (ppmv, dry basis) in the absorber, case a, [3]

4.3. The effect of adding organic acid and limestone characteristics on the wet desulfurization

The SO_2 removal efficiency of wet FGD plants using $CaCO_3$ as sorbent can be improved by the addition of various organic acids. Another way is by using a limestone type with a fine particle size distribution. In [10] the effects of adding an organic acid or using a limestone with a fine particle size distribution have been examined in a wet flue gas desulfurization pilot plant with the aim of optimization of the plant with respect to the degree of desulfurization and the residual limestone content of the gypsum. In contrast to earlier investigations with organic acids, all essential process parameters, i.e. gas phase concentration profiles of SO_2, slurry pH profiles, and residual limestone in the gypsum, were considered. Slurry concentrations of adipic acid in the range of 0–7 mM were employed. The overall degree of desulfurization in the plant increased from 83% at 0 mM to 90% at 3 mM and the residual limestone level was reduced from 4.6 to 1.4 wt%. Increasing the slurry concentration of adipic acid above 3 mM gave only a slightly higher degree of desulfurization. The wet FGD model of Kiil et al. [11] was extended to include buffer systems and verified against experimental data. It was used as a tool to identify the optimal organic acid dissociation constants (as pK_a values) and concentration levels at different operating conditions. At a holding tank pH of 5.5 and a temperature of 50°C, simulations with Bryozo limestone and a monoprotic buffer suggested that the optimum pK_a value is between 4.5 –5.5 and 5.5– 6.5 with respect to the degree of desulfurization and the residual limestone level, respectively. Adipic acid has pK_a values close to these ranges (pK_1 = 4.40 and pK_2 = 5.41 at 50°C). Changing limestone type (in the absence of organic acids) to one with a lower average particle size from 20 to 4 μm increased the overall measured degree of desulfurization from 83 to 87% and reduced the residual limestone level from 4.6 to 1.3 wt%. Increasing the holding tank pH level from 5.5 to 5.8 affected the degree of desulfurization and the residual limestone level only slightly. At holding tank pH levels between 5.88 and 5.90, a high degree of desulfurization was observed, but the residual limestone content in the gypsum increased to somewhere between 19 and 30 wt%, making this pH range unsuitable for use in a full-scale plant. A pilot plant was designed to resemble a channel in a full-scale co-current packed tower with main components a natural gas burner, a falling film column and a holding tank. Pure SO_2 is added to the flue gas, produced by the gas burner, before it enters the falling film column, a 5 m PVC tube with an inner diameter of 3.3 cm. The SO_2 is absorbed mainly in the column, but also in the holding tank. The addition of feed mixture to the holding tank is controlled by a pH unit which ensures a fixed pH in the range 5–6. Air is supplied to

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the holding tank for oxidation of HSO_3^-. The experimental work includes trials with two Danish limestone types, Faxe Bryozo and Faxe Mikrovit and various concentrations of adipic and citric acid are employed. Since in most full-scale plants chloride from the absorption of HCl is present in the slurry in varying concentrations, in the experiments a steady-state concentration level Cl^- of 25 g/l; typical for a Danish wet FGD plant, was used. This concentration was maintained by adding $CaCl_2$ $2H_2O$(s) to the feed tank. The high chloride level lowers the limestone dissolution rate, leading to an increase in residual limestone in the slurry. Figs.16 and 17 [10] show the effect of adding of organic acids on desulfurization and pH profiles in the absorber for the Bryozo limestone experiments.

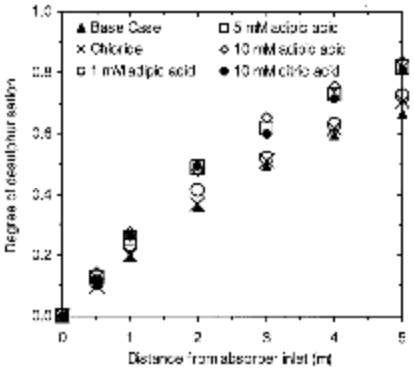


Fig. 16. Desulfurization in the absorber during trials with Bryozo limestone and organic acids, [10].

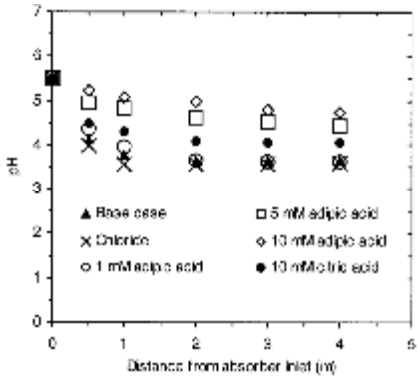


Fig. 17. pH profile in the absorber during trials with Bryozo limestone and organic acids, [10].

Another parameter of importance with regards to gypsum quality is how easily it is dewatered, [10]. The addition of citric acid in wet FGD systems decreases the gypsum particle size and might result in increased costs for dewatering of the gypsum. Adipic acid and other organic buffers provide enhanced transport of H+ in the liquid film between gas/liquid and liquid/solid. Another result of the addition of adipic acid, contributing to the enhancement of SO_2 absorption, is assumed to be an increase in the liquid/gas interfacial area in the absorber and the holding tank caused by foaming.

The sulfation properties of six different natural limestone and hydrated lime slurries were investigated in [12]. Sulfation experiments were carried out at the temperatures of 323 K and 298 K in a gaseous mixture consisting of 5% O_2, 10% CO_2, 0.5% SO_2 and a balance of nitrogen by volume. Total sulfation capacities of the slurries were found to vary depending on sulfation temperature, sorbent properties and the sorbent content of the slurry. It was determined that the total sulfation capacities of all slurries shifted to higher values as the $CaCO_3$ and $Ca(OH)_2$ contents of sorbents and sorbent content of slurries increases and sulfation temperature decreases. Depending on sulfation conditions and the sorbent properties, the total sulfation capacities of limestone and hydrated lime slurries varied between 14.0-33.1 (mg SO_3/ml slurry) and 17.4-40.4 (mg SO_3/ml slurry), respectively. Regression analysis was used to relate the total sulfation capacity values to the $CaCO_3$ and $Ca(OH)_2$ contents of sorbents and linear empirical equations were developed.

4.4. Modeling of desulfurization process on the basis of equilibrium and mass transfer in Ca^{2+}- SO_2 - H_2O system [13]

An industrial desulfurization process is modeled in [13] on the basis of equilibrium data, mass balance, mass transfer and plant data. For the Ca^{2+}-SO_2-H_2O system the equilibrium diagram at 25 °C is constructed. The diagram presents the concentration of total SO_2 combined SO_2, true free SO_2, the pH value and the solubility curve for $CaSO_3.1/2H_2O$. Besides the basic chemistry occurring in the

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process, the role of relevant additional chemical species is explained. The overall desulphurization process is studied through the analysis of the partial processes: absorption of SO_2 and sulfite to bisulfite reaction; limestone dissolution and its reaction with $Ca(HSO_3)_2$; absorption of O_2, oxidation of $CaSO_3$ and gypsum crystallization mass balance and the mass transfer. The model is tested on the basis of data taken from an industrial plant. The equilibrium diagram, Fig. 18, is used for a graphical presentation of the three partial processes occurring in the industrial desulphurization process—absorption of SO_2 and sulfite to bisulfite reaction; limestone dissolution and its reaction with $Ca(HSO_3)_2$; absorption of O_2, oxidation of $CaSO_3$ and gypsum crystallization. The design diagram, Fig. 19, is used to present the process of absorption of SO_2 and is also a useful tool for calculating the mass transfer.

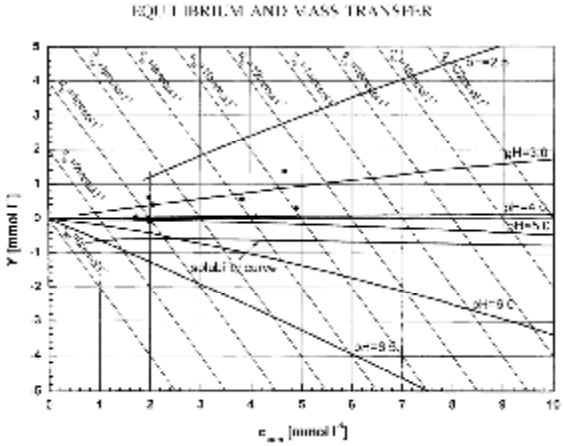


Fig. 18. Equilibrium diagram for the Ca^{2+}-SO_2-H_2O system at 25°C. At the experimentally confirmed points the pH prediction was within 0.1 of the measured value, [13, Fig. 1].

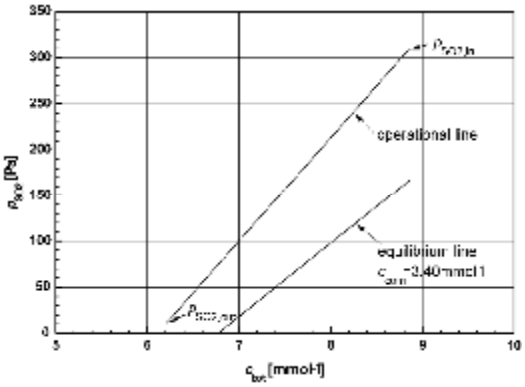


Fig. 19. Design diagram for the Ca^{2+}-SO_2-H_2O system at 25^{O}C; presentation of the partial process of absorption of SO_2, [13, Fig. 5].

Here $Y=c_{tot_} - 2\,c_{com}$, $c_{com} = c_{SO_3^{2-}} + 0.5.\, c_{HSO_3^-}$, $c_{tot} = c_{SO_2} + c_{SO_3^{2-}} + c_{HSO_3^-}$.,

where c is concentration and the subscripts denote: tot- total SO_3; com –combined SO_3; SO_3^{2-}, SO_2, HSO_3^- - species. The mass transfer analysis for all three partial processes has also been carried out. The results of the mass transfer analysis have been verified by the basic mass balance and the overall reaction, and they are within a 10% margin. The developed model is found to be an acceptable tool for the industrial desulphurization process analysis. A sensitivity analysis of various parameters used in the mass transfer calculations is carried out. The values are changed by ±20% and the influence of the change on the results of the mass transfer calculation is observed. It has been concluded that the interfacial area, which is calculated by the droplet, limestone particle or bubble diameter is of great importance when considering the possibilities of improving the mass transfer. Namely, the interfacial area can be enlarged by decreasing the droplet, limestone particle or bubble diameter, which is in the process achievable by modifying or changing the nozzles or by finer limestone grinding. The height of the layer of the suspension in the holding tank also has a significant influence on the molar flow of the limestone.

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4.5. Use of spray dry absorption product as a sorbent in WFGD plants [14]

Since the sulfite content of the spray dry absorption product (SDAP) is the main obstacle against this material's useful application, it could be a possibility to oxidize SDAP in wet FGD plants [14]. An experimental investigation of the effects on plant performance of converting SDAP to gypsum in a wet flue gas desulfurization (FGD) pilot plant, based on the falling film principle, has been conducted in [14]. At concentrations up to 300 g SDAP/l (feed tank basis), no scaling or plugging of pipes was observed. The SO_2 removal efficiency increased from 69 to 76.5% when increasing the concentration of SDAP in the feed tank from 0 to 300 g/l. At the same time, the average limestone slurry feed rate decreased from 1.62 to 0.53 l/h as a consequence of the residual content of $Ca(OH)_2$ and $CaCO_3$ in the SDAP. The compounds, $CaCl_2 \cdot 2H_2O$, NaF, CaF_2 and $Al(OH)_3$ were added, in various concentrations, to the feed tank to investigate the effects of Cl-, F-, and Al_3+ on the limestone reactivity. The degree of desulfurization (in the presence of 200 g SDAP/l) increased from 75 to 78% with an increase of Cl^- concentration from 0 to 30 g/l and simultaneously the residual limestone content of the gypsum increased from 2.8 to 15.8 wt%. The investigation has shown that SDAP can be used as a sorbent in wet FGD plants and the sulfite converted to gypsum, but the observed increase in the residual limestone level of the gypsum may give some problems in utilization of the product.

4.6. Investigations of the effects of operating parameters on desulfurization efficiency

The difficulty in the prediction of the SO_2 removal from flue gas by WFGD is that the performance of the system is related to a wide range of variables, [15]. Investigations of the effects of the operation parameters on SO_2 removal efficiency are commented below.

An experimental parameter study was conducted [16] in a pilot-scale jet bubbling reactor, Fig. 20 for wet flue gas desulphurization. The pilot plant is downscaled from a limestone-based, gypsum producing full-scale wet FGD plant. Important process parameters, such as slurry pH, inlet flue gas concentration of SO_2, reactor temperature, and slurry concentration of Cl^- have been varied. The degree of desulfurization, residual limestone content of the gypsum, liquid phase concentrations, and solids content of the slurry were measured during the experimental series. The SO_2 removal efficiency increased from 66.1% to 71.5% when the reactor slurry pH was changed from 3.5 to 5.5. Addition of Cl^- in the form of $CaCl_2$ $2H_2O$) to the slurry (25 g Cl^-/l) increased the degree of desulfurization to above 99%, due to the onset of extensive foaming, which substantially increased the gas–liquid contact area. An increase in the inlet flue gas SO_2 concentration from 502 to 991 ppmv led to a decrease in the SO_2 removal efficiency from 80.1% to 69.4%. A temperature increase from 296 to 323 K caused a reduction in the degree of desulfurization from 69.4% to 68.1%, but this result is almost within the experimental uncertainty. The residual limestone level in the gypsum formed increased with increasing values of reactor slurry pH, inlet flue gas SO_2 concentration, and slurry Cl^- concentration.

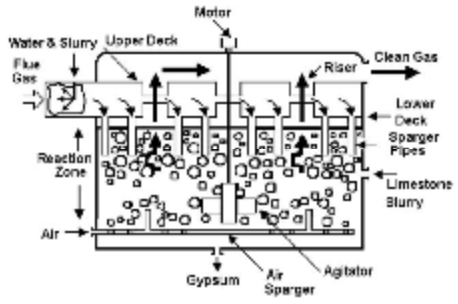


Fig. 20. Schematic illustration of a full-scale jet bubbling reactor, [16, Fig. 1].

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The effects of operating parameters on desulfurization efficiency of a dual-alkali FGD process in a rotating-stream-tray (RST) scrubber Figs. 21, 22 are investigated experimentally in [17] and presented in Fig. 23. A dimensionless factor, ε, is proposed in this study to predict desulfurization efficiency of this dual-alkali FGD system. ε presents the desulfurization ability of a dual alkali FGD system, determined by five main operating parameters such as sodium ion concentration, ratio of absorbent flow rate to flue gas flow rate, pH value of absorbent solution, ratio of sulfate ion to total sulfur ion in absorbent solution, and sulfur dioxide concentration of inlet flue gas. The empirical expression for predicting desulfurization efficiency at different temperatures is obtained through the experimental study and theoretical calculation. It provides useful guide for engineering design.

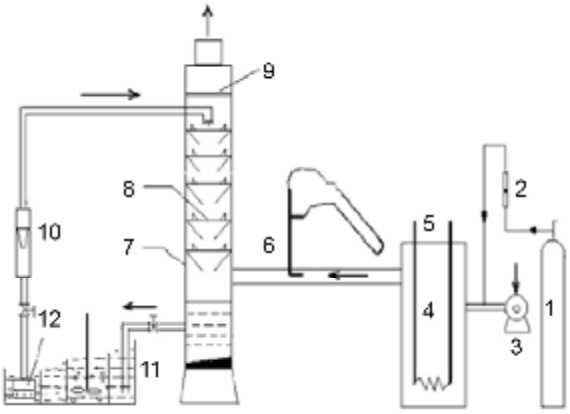


Fig. 21. The experimental setup of dual-alkali FGD. 1. Pure sulfur dioxide tank, 2. Gas rotameter, 3. Centrifugal fan, 4. Buffer tank, 5. Electronic heat pipe, 6. Pitot tube, 7. Rotating-stream-tray scrubber, 8. Rotating-stream-tray, 9. Mist eliminator, 10. Liquid rotameter, 11. Cycling tank, 12. Pump. [17, Fig.1]

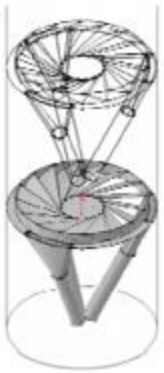


Fig. 22. RST structure [17, Fig.2]

In [15], the SO_2 was removed by absorbing and reacting SO_2 with limestone slurry, and limestone scrubbing was accomplished in a spraying reactor. Experimental investigations for effects of different operating variables on the SO_2 removal showed the reasonable process parameters such as the pH value of the liquid phase, droplet size of the spray and the flow rates of liquid and gas. The removal process was analyzed using the two-film theory of mass-transfer. Both the liquid and gas side resistances were important, and the absorption rate was controlled by a combination of both gas-film and liquid-film diffusion controls. A model of external mass-transfer with the effects of a chemical enhancement factor and sulfite concentration in the liquid phase was developed for the prediction of the SO_2 removal efficiency, and the calculated values were in reasonable agreement with the experimental values. The study is considered as the one-dimensional prediction of SO_2 removal and low-cost application of limestone slurry for commercial FGD technology. The reactor consists of the spraying absorber of 0.5 m in diameter and 1.20 m in height and product oxidization tank. The impeller in the tank was rotated at 300 min^{-1} in order to efficiently mix the gas, liquid and solid phases in order to favor the oxidation of desulfurization products.

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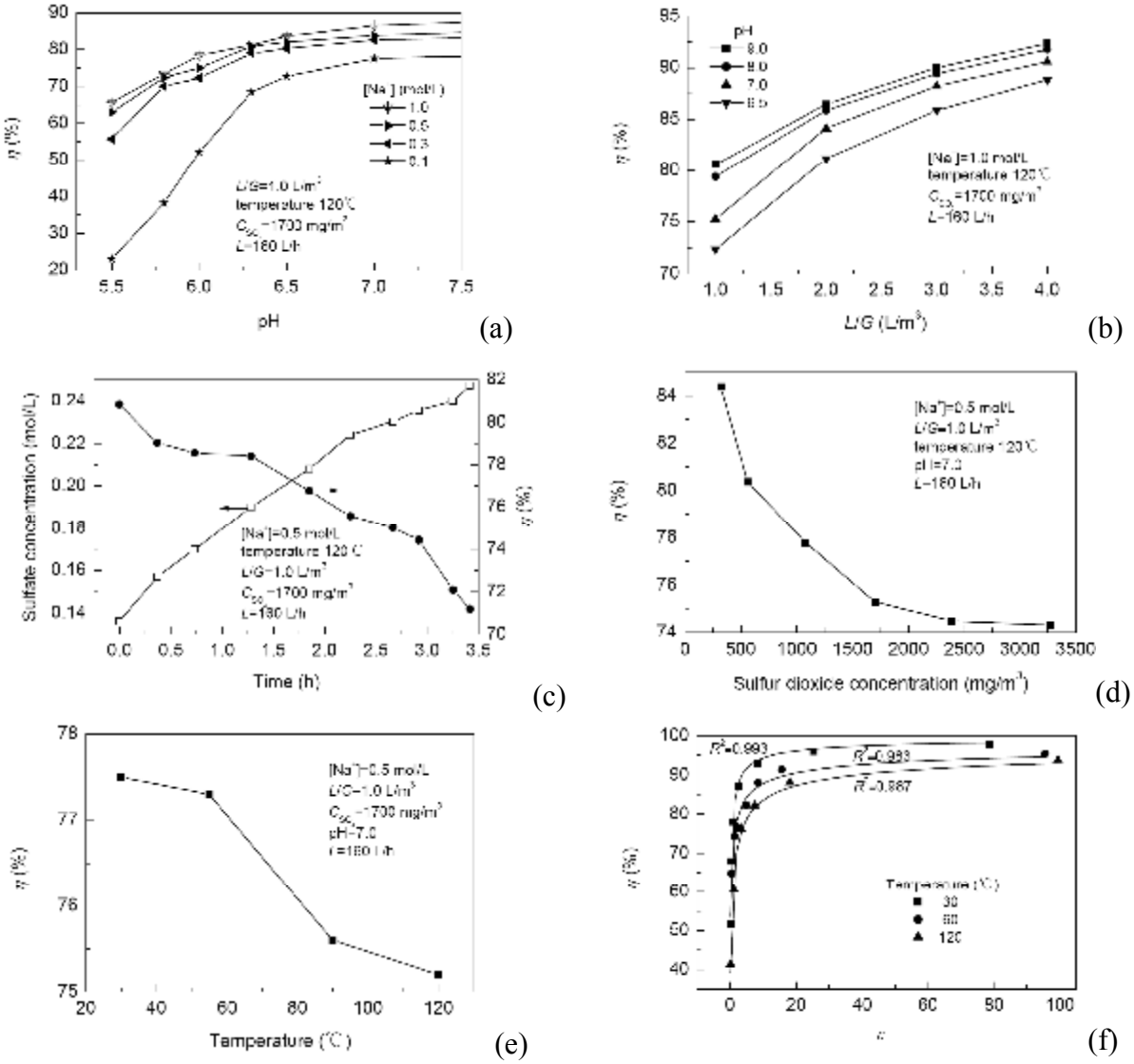


Fig. 23. Effects of the main process parameters: (a)- sodium ion concentration, (b)- L/G, (c)- sulfate ion concentration, (d)- SO_2 concentration, (e)- gas temperature and (f)- ε on the SO_2 removal efficiency η, [17, Figs. 3-8]

The droplet sizes were recorded with a charge-coupled device camera. Experiments were first carried out to test effects of slurry pH and limestone concentration on both SO_2 removal efficiency and residual limestone content of the gypsum with the nozzle of the average droplet size of 500 μm and the desulfurization conditions of the gas flow rate of 5 l/min (Q_G) and the liquid flow rate of 50 ml/min (Q_L). The mole ratio of liquid to gas phase (L/G) is about 12.5 at the gas flow rate of 5 l/min and the liquid flow rate of 50 ml/min. the SO_2 removal efficiencies increased with increasing the limestone concentration, and it was 85% at the limestone concentration of 11 wt.% and increased to 95% at the limestone concentration of 18 wt.%. Thus, the limestone concentration of higher than 15 wt.% should be expected to obtain desirable SO_2 removal efficiency, however, residual limestone content of the gypsum was higher than 0.008 for the limestone concentration of higher than 15 wt.%. Fig. 23(a) illustrates the SO_2 removal efficiencies increased with increasing the pH value of slurry from 5.0 to

6.0. At normal operating conditions, the pH is controlled at about 5.5. When the pH was too high, the SO_2 absorption was enhanced, but the concentrations of both SO_3^{2-} and CO_3^{2-} increased so that $CaCO_3$ and $CaSO_3$ easily crystallized on the absorbent surface, which prevented further absorption and reaction with the absorbent. Absorption of SO_2 at low pH increases absorbent utilization efficiency and eliminates sulfite ions that produce scaling and plugging. From an economic point of view, the mole ratio of liquid to gas, L/G has been found to be one of the most important criterions for reporting the reactor performance, [18]. In practical FGD process, the L/G value is selected by its minimum value, which was expressed, [15]:

$$\frac{L}{G} = (1.1-2)\left(\frac{L}{G}\right)_{\min},$$

where

$$\left(\frac{L}{G}\right)_{\min} = \frac{(P_{A1}-P_{A2})}{(c_1^*-c_2)}\cdot\frac{c_M}{P_T},$$

where P_{A1}- partial pressure of SO_2 in gas phase at inlet, atm; P_{A2}- partial pressure of SO_2 in gas phase at outlet, atm; c_1^* is the outlet SO_2 equilibrium concentration in liquid phase, kmol/m^3; c_2 is the inlet SO_2 concentration in liquid phase, kmol/m^3; P_T is the overall pressure, atm; and c_M is the overall concentration in liquid phase, kmol/m^3, calculated by:

$$C_M = \frac{\rho_L}{M_M},$$

where ρ_L is the liquid phase density, kg/m^3 and M_M is the mole mass of the liquid phase, kg/kmol.

In this study $(L/G)_{\min}$ was calculated as 9.0.

4.7. Milliken Clean Coal Technology Demonstration (MCCTD) Project- testing of Saarberg-Hölter-Umwelttechnik (S-H-U) FGD technology [19]

In October 1992, the New York State Gas & Electric Corporation (NYSEG) entered into a cooperative agreement with U.S. Department of Energy to conduct a study [19] and to jointly fund the project, consisted of installing nitrogen oxides and sulfur dioxide -reduction technologies on units 1 and 2 at Milliken Station. Each unit has a rated capacity of 150 MWe, for a total station capacity of 300 MWe. Construction for the demonstration project began in April 1993. Operating over 30 000 hours during 3½ years, this project was very successful, yielding substantial environmental benefits in the form of emissions and waste reductions. Its operational success is validated by the continued use of equipment to lower emissions from the Milliken Station. The heart of MCCTD Project is the S-H-U FGD technology, Fig. 24. Although the S-H-U process was developed and tested in Europe, this project represents the first test on a boiler burning U.S. coals, which have significantly different properties and trace contaminants than European coals. Installation of the S-H-U technology was expected to achieve the following: Up to 98% SO_2 removal by operation of a two-stage cocurrent/countercurrent absorber; Low limestone reagent consumption; Excellent process stability and ease of operations during load changes and other operational transients; Closed-cycle operation with essentially no liquid waste discharge; Freedom from scaling and plugging in the absorber and associated equipment; High absorber availability and low maintenance; Production of commercially salable by-products; Improved energy efficiency compared to other FGD technologies; Ability to operate at high-chloride concentrations without adversely affecting SO_2 absorption efficiency.

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The conclusions reached from a test, run on Unit 2 with low sulfur coal with a sulfur content of 1.6 %, were: SO_2 removal ranged from 30 %, using only two spray headers without formic acid addition, to 98 %, using all seven spray headers and formic acid at a concentration of 800 ppm; Adding formic acid significantly enhanced SO_2 removal. With five spray headers in operation, SO_2 removal increased from 82 % without formic acid to 97 % with 800 ppm of formic acid; With all seven spray headers in operation, SO_2 removal was 90.2 % at a pH of 4.21 and increased to 94.4 % at a pH of 5.05; On average, SO_2 removal increased 2.6 % when a finer limestone grind size (90 % through 325 mesh compared to 90 % through 170 mesh) was used; At equivalent L/G ratios, the unit performed better at high gas velocity than at design velocity, i.e., at a given L/G, higher mass-transfer rates were achieved at gas velocities above the design value; Changing the L/G ratio in the cocurrent section had no measurable effect on pressure drop, but increasing the L/G ratio in the countercurrent section significantly increased the absorber pressure drop; Mass transfer (and, consequently, SO_2-removal rate) increased with increasing L/G, but the effect was not necessarily linear ; Formic acid increased the mass transfer rate, but the effect was not linear and diminished with increasing formic acid concentration; There is little effect of chloride level on SO_2-removal efficiency as long as chloride concentration is below about 5 % (50 000 ppm).

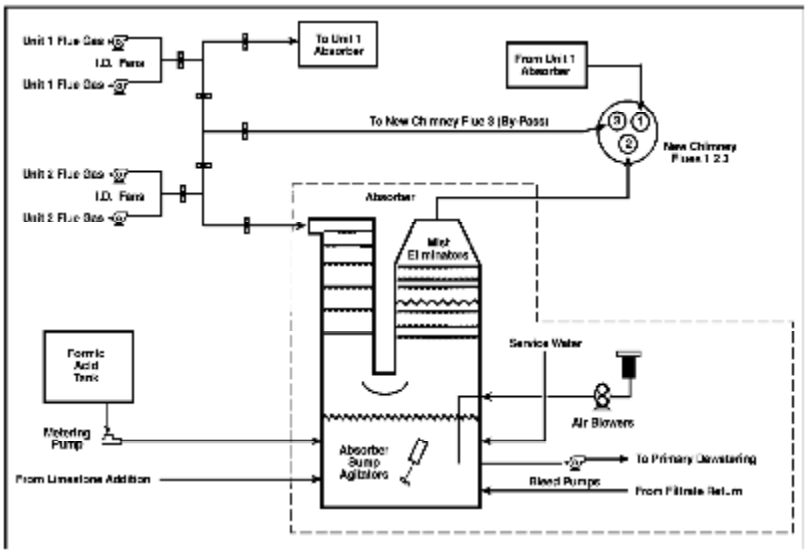


Fig. 24. S-H-U Flow Diagram [19, Fig. 2]

4.8. Developments in monitoring and control of FGD systems

In limestone-gypsum FGD systems, the consumption of a desulfurization agent (lime) is controlled using online pH analyzers, Fig. 25. Of great concern in the pH measurement is heavy lime scaling on the pH electrode. To ensure accurate measurements, frequent cleaning of the electrodes with acid is required, adding to both maintenance workload and cost. The presented in [20] chemical cleaning system automates the acid cleaning process, which not only saves both time and expense but also ensures precise pH measurement over long periods. The expected benefits are: Improves the efficiency of a limestone-gypsum FGD system; Ensures stable, continuous pH measurement; Reduces operating costs; Eliminates manual cleaning.

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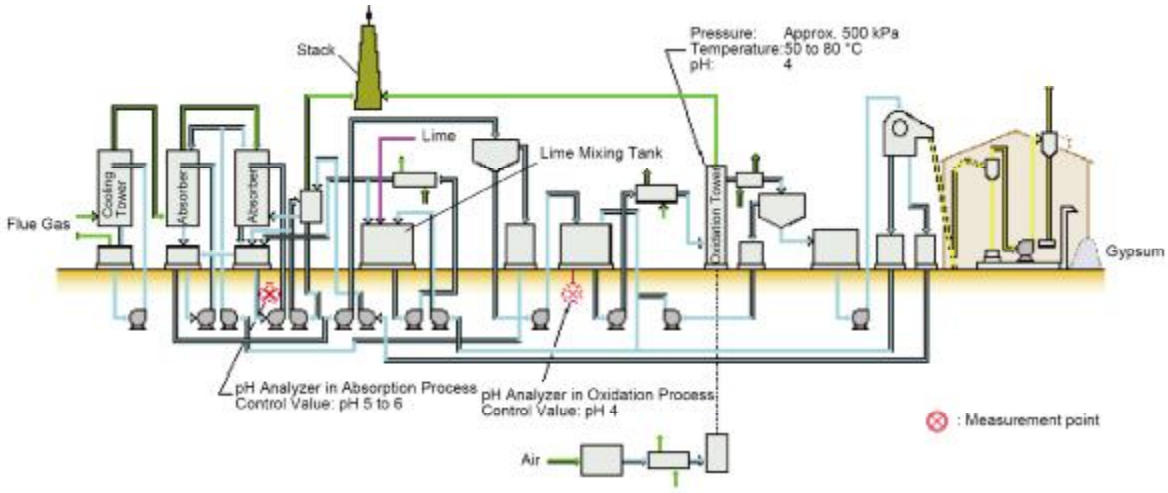


Fig. 25. pH measurement points for control of limestone-gypsum FGD systems [20].

A method for real time detection of the oxidation status for more efficient FGD is proposed in [21]. The method pertains to a wet scrubber that uses lime or limestone as a reagent for a FGD system with natural or forced oxidation. The method comprises locating a monitor in the system for accessing the slurry. A sample is periodically drawn from the slurry by the monitor wherein a titration is performed on each sample, which comprises adding a potassium iodate KIO_3 solution, a potassium iodide KI starch solution and an acid (H_2SO_4) to the sample in the monitor for causing the sample to exhibit a color corresponding to the oxidation rate. The optical system measuring the change of the color uses light source operating at a wavelength of 400-500 nm and an optical sensor measuring the intensity of the light as compared with a reference.

A method is proposed in [22] for gypsum WFGD by bringing the flue gas into contact with a recycling slurry containing a calcium compound in an absorbing tower, blowing a gas containing oxygen into the slurry and successively detecting an oxidation-reduction potential (ORP) of the slurry; whereby a flowrate of the gas containing oxygen is regulated so as to completely oxidize calcium sulfite in the slurry. ORP is loyally concerned with the concentration of sulfurous acid in the liquid and will indicate a low value even at extremely small amount of sulfurous acid, Fig. 26. Experimental results for the relation between the concentration of sulfurous acid in the recycling liquid and a flow rate of air, which is fed into a liquid tank disposed in the lower portion of an absorbing tower are presented in Fig. 27. It is seen that as the air flow rate is increased an oxidation rate will be accelerated and the concentration of sulfurous acid will thus be lowered. The ORP can be easily measured by dripping platinum electrodes in the recycling liquid in the liquid tank.

4.9. Modeling SO_2 absorption into $CaCO_3$ suspensions with the film theory

In [23] the absorption of SO_2 from mixtures with N_2 into limestone slurries has been studied. The aim is to determine the applicability of modeling SO_2 absorption into $CaCO_3$ suspensions by examining the transference of the SO_2 from the gas bulk to that of the slurry and by taking into account instantaneous reactions between ions. This was done by making an experimental study of SO_2 absorption using a reactor that provided a limited contact time between the gas and the slurry, in order to avoid the influence of the dissolution rate of solid particles.

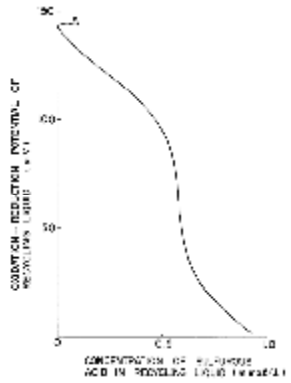


Fig. 26. ORP versus concentration of sulfurous acid in recycling liquid [22, Fig. 1]

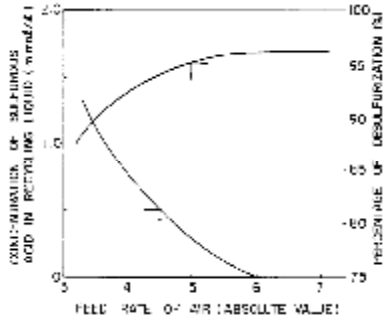


Fig. 27. Relation between the concentration of sulfurous acid in the recycling liquid, the flow rate of air fed into the liquid tank and desulfurization efficiency [22, Fig. 2]

The model developed in [24], which applied the film theory, has been extended to consider the case when the desorption of CO_2 may also be taken into account. The reactor used was a stirred tank with an almost flat gas–liquid interface of area 67.7×10^{-4} m^2 at 400 min^{-1}, operated in gas-phase continuous operation mode and batchwise for the slurry. The operating temperatures used were 20°C and 40°C, the content of limestone in the initial slurry was 1.3 and 5 wt% and the volume fraction of SO_2 in the gas mixture at the inlet to the reactor ranged from 4% to 10%. The overall gas-side SO_2 transfer coefficient has been determined, obtaining values of 0.104 and 0.083 mol/(s.m^2.bar) at 20°C and 40°C, respectively. By taking into account the individual gas-side SO_2 transfer coefficient and estimating the enhancement factor, the thickness of the interfacial liquid film, 45 and 58 μm at temperatures of 20°C and 40°C, respectively, and the SO_2 physical absorption coefficient, 3.27×10^{-5} and 4.01×10^{-5} m/s at 20°C and 40°C, respectively, have been determined. The results obtained are comparable with those reported in previous studies. A calculation procedure has been developed that uses the values for the limestone content in the initial slurry, the total SO_2 in the liquid phase and the pH to determine the concentrations of all the species. The experimental values demonstrate the considerable reduction in the absorption rate as the $CaCO_3$ disappears from the slurry, and that the flux of SO_2 across the gas–liquid interface does not vary significantly with the operating temperature, therefore the reactions are instantaneous and the process is limited by a physical step.

4.10. Developments on calcium sulfite/bisulfite oxidation process of WFGD

A large scale Computational fluid dynamics simulation study [6] has been performed with the aim to optimize the design of the oxidation tank (at the bottom of the scrubber) of a wet FGD process with obtaining of gypsum for the purpose of savings in investments and operation costs. A commercial CFD program Fluent 5.5 was adopted including user submodels for bubble size distributions, mass transfer, physical properties and reaction kinetics. The details of the case simulation are as follows: oxidation vessel diameter 13.12 m, vessel height 25.7 m, liquid level (calcium sulfite/bisulfite containing slurry from the absorber above) height 9.24 m, flue gas flow in is 2 000 000 kg/h containing 4 000 kg/h sulfur dioxide, oxidation airflow is 8 000 kg/h and gypsum (10% moisture content) is produced 11 000 kg/h. The oxidation tank is large, several thousand cubic meters in volume. The content of solids in the slurry is typically from 15-26 %. Side entering mixers in the tank are used to provide enough flow and to prevent the solids from settling to the bottom. A number of side- entering impellers aid the oxygen mass transfer from the air bubbles to the solution. Average power consumption of this type of desulfurization process is about 1-1.5% of the total power plant

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energy output. Typically the WFGD process provides 90-98% desulfurization degree. Gypsum purity is normally around 95%, but depends on the limestone quality.

A method of FGD is proposed in patent [25] wherein a flue gas is contacted in a liquid scrubber unit with and aqueous slurry formed from calcium hydroxide and magnesium hydroxide and which contains magnesium hydroxide present in an amount to provide an effective magnesium ion content between 2500 to 9000 ppm in the scrubber. As known the effective amount of magnesium ion content is that amount over and above the chloride ion content of the aqueous medium present in the scrubbing unit. The calcium sulfite in the discharge from the scrubbing system is oxidized to gypsum. The sulfite is oxidized in a thickener overflow at pH of between 4-6.5 to a calcium sulfate which precipitates from the aqueous media and is separated, while the aqueous media is recycled to an acidification step preceding the oxidation. The slurry from the scrubbing tower is thickened to separate undissolved calcium sulfite, in a sludge containing at least about 20 wt% total solids, from the slurry. The discharge is acidified with sulfuric acid or other aqueous acid to cause dissolution of calcium sulfite in an aqueous solution. The pH of the solution is preferably between about 5.2-5.5 which will provide for preferred crystal size formation, no gaseous sulfur dioxide release and easy operation with about 99 % oxidation in the following step of the process. In preferred practice the calcium sulfite is dissolved in mixing tank during a nominal residence time of 0.5-1.5 hours. In –line pH analyzers on the liquid outlet line from the mixing tank and from the oxidizing tower may be used to control the addition of acid.

In patent [26] a constructive solution is proposed providing an in-situ forced oxidation retrofit for wet flue gas scrubber in which the sparge pipes delivering the oxidation air are mounted inside the absorber tank making either one or no penetrations of the tank wall nor adding any loads on the walls of the tank. The system is intended for both integrated and open recirculation tank. The retrofit system, Fig. 28, consists of a main air header (2) that feeds the sparge pipes (3).The main header forms a loop that extends above the liquid level (1) in the tank, forming an upflow leg (4) of the main header. The leg prevents back flow of the tank contents to the compressors. This is more reliable than the usual use of check valves.

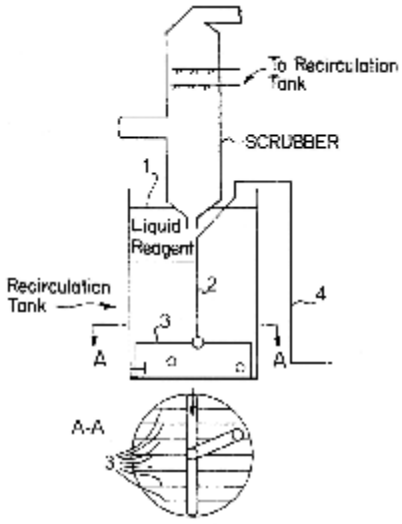


Fig. 28. WFGD scrubber with an open recirculation tank [26]. (1)- liquid level, (2)- main air header, (3)- sparge pipes, (4)- upflow leg.

4.11. Prediction of SO_2 absorption.

Variety of models is developed for prediction of SO_2 absorption in WFGD systems.

WFGD systems using lime as a reactant involve neutralization and recirculation of the absorbent slurry that contains particles of calcium sulfite hemihydrate and gypsum. At sufficiently high pH, the effective reactant in the absorption section is solid calcium sulfite [27]. The absorption rate of SO_2 into calcium sulfite slurries is predicted in [27] by means of a model, based on the film theory, which considers absorption in a liquid film located at the gas-liquid interface and simultaneous dissolution of calcium sulfite in a liquid film surrounding the particles. The involved reactions are supposed to be reversible and instantaneous. Diffusive transport of ionic and molecular species in both films accounts for the effect of equilibrium and, due to unequal diffusivities of ions, for the effect of the electric potential gradient. Predicted overall gas mass transfer coefficients and mean absorption rates were found to be in good agreement with experimental values obtained at different conditions in a cable contactor.

In [28] a thermochemical model has been proposed for the modeling of the flue gas cleaning system of a Refuse Derived Fuel (RDF) incineration power plant. The combustion includes the grate incinerator and the post-combustion chamber, while the cleaning section includes the NOx reduction process (urea injection) and the scrubbing of SO_2 and HCl ($Ca(OH)_2$ as sorbent). The modeling has been conducted by means of ASPEN PLUS code able to evaluate many different chemical processes and estimate energy and mass balances. The model can be a useful tool in both evaluating the efficiency of the gas cleaning system and in forecasting the efficiency of the cleaning system in off-design operating conditions. The model has been developed according to the design data (mass flows, RDF composition and plant components) of the plant manufacturer. The simulation results have been validated with the experimental data available.

In [29] a model based on the penetration theory has been developed to calculate the dynamic absorption rate of sulfur dioxide into a droplet of limestone slurry. The model includes both instantaneous equilibrium reactions and reactions with finite rates; limestone dissolution, sulfite oxidation, gypsum crystallization and the hydrolysis reaction of CO_2. The model has been used to quantify the mass transfer within a spray scrubber and to estimate the impact of the reactions with finite rate of the SO_2 mass transfer.

4.12. Studies on the kinetics of oxidation of calcium bisulfite

In wet limestone scrubbing, oxidation of calcium bisulfite plays a major role both by determining the dewatering properties of the obtained sludge and the production of gypsum of high quality [30, 31, 32]. This process requires, downstream of the absorber, a hold tank where crystallization of $CaSO_3$ and $CaSO_4$ and dissolution of make-up $CaCO_3$ occur [32]. Forced oxidation of sulfite in the hold tank allows the main problem of the process to be solved i.e. the disposal of the solid by-product, a sludge composed of calcium sulfite and sulfate. Forced oxidation is carried out by injecting air into the liquid phase, so that the following reactions take place:

$$HSO_3^- + \frac{1}{2}O_2 = SO_4^{2-} + H^+$$

$$SO_3^{2-} + \frac{1}{2}O_2 = SO_4^{2-}$$

The kinetics of such reactions, and particularly of the absorption of oxygen by basic solutions of sodium sulfite in presence of catalysts, received much attention during the last 30 years; [33] presented a detailed review of the literature for the period 1960-1980. The researchers who studied the reaction of sulfite oxidation pointed out the extreme sensitivity of its kinetics to experimental conditions. It has

been shown that liquid-phase composition (sulfite concentration, dissolved oxygen, pH), temperature, and the presence, even in traces, of catalysts (Co^{2+}, Cu^{2+}, Mn^{2+}) and inhibitors (alcohols, phenols, hydroquinone) strongly affect the reaction rate. The kinetics of sulfite oxidation was studied in homogeneous conditions or in heterogeneous conditions. Results for homogeneous conditions, obtained by contacting a sulfite solution with an oxygen saturated solution, are relatively consistent, indicating a 3/2-order dependence from sulfite and a zero-order dependence from oxygen, both in the absence and in the presence of catalysts [32].

4.12.1. Uncatalyzed oxidation

In order to contribute to the simulation of the wet limestone FGD process, in [31] comprehensive model for prediction of uncatalysed calcium bisulfate oxidation in a isothermal gas–liquid stirred tank reactors has been used. Based on the assumption that the reactions are zeroth order with respect to gaseous reactants, the model requires appropriate physico-chemical parameters which are taken from the literature. The model was used to quantitatively interpret some literature experimental data. In particular, the model is capable of confidently predicting the transition from chemically to mass transfer controlled regime occurring when changing the operating conditions.

In [32] the oxidation rate was experimentally studied by contacting pure oxygen or mixtures of oxygen and nitrogen with calcium bisulfate solution. The experiments were carried out in a well-mixed bubbling reactor varying temperature oxygen partial pressure and sulfite concentration, in the absence of solid calcium sulfite and of catalytic species. It was shown that the rate of the process is controlled by reaction kinetics, and that the reaction rate is zero order in dissolved oxygen and 3/2-order in bisulfite ion. Some of the results from literature relative to sulfite oxidation in conditions typical of FGD processes are reported in Table 1. The table shows that the interpretation of the experimental results is somewhat contradictory probably due to the interactions between the reaction steps on the one side, and the diffusive transport of reactants, products and catalysts on the other.

The analysis of the experimental results is made complex by the problem of finding out whether oxygen absorption takes place in the fast reaction regime or in the diffusional or kinetic reaction subregimes. With this aim it is necessary to compare the experimentally measured reaction rate to the rate characteristic of the diffusional subregime, r_D, since, if the reaction rate $r >> r_D$, , it can be assumed that the process takes place in the fast reaction regime, while if $r << r_D$, it can be assumed that the process takes place in the kinetic subregime With few exceptions $r < r_D$, and this indicates that the process takes place in the kinetic subregime. The experiment is carried out in a laboratory isothermal gas–liquid stirred tank reactor presented in Fig. 29

Table 1. Literature results for the sulfite oxidation kinetics in FGD conditions

Authors	***T*** **°C**	**pH**	***S(IV)*** **order**	***0_2*** **order**	***H^+*** **order**	***Mn^{2+}*** **order**
Weisnicht *et al.* (1980) [34]	40	4.6-5.0	3/2	-	-	-
Pasiuk-Bronikowska and Bronikowski(1981), [35]	40	<3	0	0-1	- 1-0	0-2
Huss *et al.* (1982), [36]	25	1-4	0-1	0	-	1-2
Pasiuk-Bronikowska and Bronikowski (1989), [37]	26	1.5	0	1	-	2
Ulrich *et al.* (1986), [38]	25-75	4-5	0	0-1	-	1/2
Pasiuk-Bronikowska and Bronikowski (1989), [39]	26	3.9-4.8	0	1	-	0
	26	4.8-6.6	3/2	0	-	1/2
Pasiuk-Bronikowska and Ziajka (1989), [40]	26	4.5-6.0	3/2	0	0	1/2
	26	3.8-4.2	0	1	0	0

Note: The dash indicates that the dependence is not studied.

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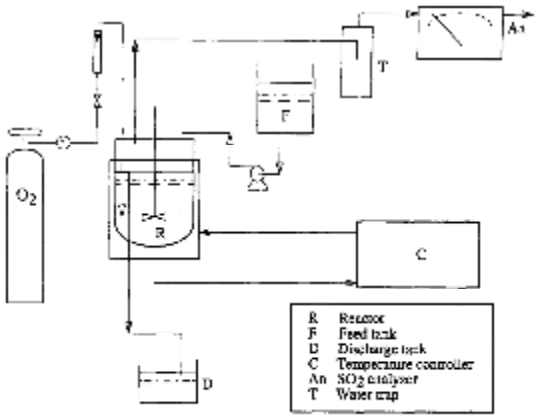


Fig. 29. Sketch of the experimental apparatus [32, Fig. 1].

In Figs. 30 and 31 the reaction rate is reported as a function of HSO_3 concentration; in particular, Fig. 30 refers to the runs carried out using pure oxygen and varying the experimental temperature, while Fig. 31 refers to the runs carried out at 45°C with different oxygen partial pressures. In Fig. 30 together with the experimental results, three straight lines of slope 3/2, obtained from the kinetic law considering the three temperatures of 25, 45, 63°C are reported. On the other hand, in Fig. 31 just one single straight line is capable of describing the experimental results relative to pure oxygen and to the mixtures containing 40 and 21% oxygen, confirming that sulfite oxidation is zero order in oxygen. However in such a figure three straight lines are also reported relative to the "diffusional" rates corresponding to 100, 40, and 21% oxygen. Such lines clearly indicate that the diffusional rate constitutes an upper limit for the oxidation rate at the transition between the kinetic and the diffusional subregimes. This kinetic equation appears to confirm the chain mechanism proposed by Bäckstrom [41]. However, the problem remains open of clarifying whether 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. The fact that in industrial applications some metallic ions are present, which come as impurities of limestone and may have a catalytic activity on sulfite oxidation, suggests the opportunity of extending the study [32] to the oxidation reaction in the presence of catalysts.

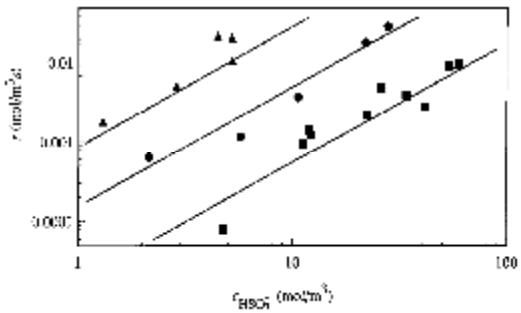


Fig. 30. Reaction rate vs HSO_3^- concentration for experiments carried out with pure oxygen and temperatures of 25, 45, and 63°C. ■ : 25°C; ●: 45°C; ▲: 63°C. [32, Fig. 2]

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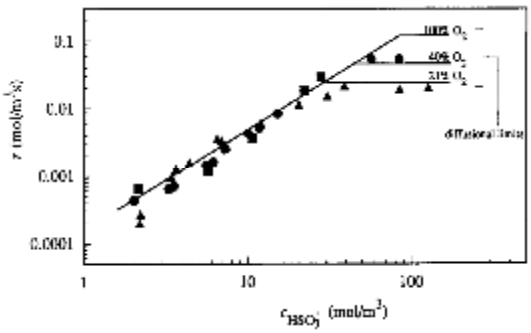


Fig. 31. Reaction rate vs HSO_3^- concentration for experiments carried out with temperature of 45°C and oxygen concentrations of 100, 40, and 21%. ■: 100% O_2; ●: 40% O_2; ▲: 21% O_2. [32, Fig. 3]

4.12.2. Catalyzed oxidation

A model is proposed in [30] to describe interaction between mass transfer and chemical reaction in the process of sulfite oxidation under heterogeneous conditions (i.e. in which gaseous oxygen and sulfurous solution are brought in contact). It considers the characteristics of absorption with zero order reaction. A kinetic equation of order 3/2 with respect to both catalyst concentration and sulfite concentration was used, allowing the evaluating of oxygen absorption rate as a function of catalyst concentration.

The calcium bisulfite oxidation in wet limestone FGD in the presence of catalysts is studied experimentally in the works of the same authors [42-46] with the laboratory-scale apparatus used in [32], Fig. 29.

In the previous work [32] it is shown how the following equation appears to be the most appropriate to describe the kinetics of the oxidation reaction for a pH range of 7.5-9 in homogeneous conditions:

$$r = k c_M^{1/2} c_{S(IV)}^{3/2} \quad (1)$$

where r is the reaction rate expressed as moles of SO_4^{2-} produced per unit time and volume, k is the kinetic constant, c_M is the catalyst concentration, and $c_{S(IV)}$ is the total sulfite concentration. Eq. (1) can be interpreted by assuming that the reaction takes place via a free-radical mechanism, with a chain initiated by the catalyst autoxidation or by the action of UV light. On the other hand, in both homogeneous and heterogeneous oxidation, the reaction is highly sensitive to operative conditions, such as the liquid phase composition (sulfite concentration, dissolved oxygen, and pH) and the presence, even in traces, of catalysts (Co^{2+}, Cu^{2+}, Mn^{2+}, and Fe^{2+}) and inhibitors (alcohols, phenols, and hydroquinone). The previous experimental study [32] of the bisulfite oxidation reaction in heterogeneous conditions has given the kinetic equation for calcium bisulfite oxidation that follows, which is of zero order in oxygen and three halves in HSO_3^- ions:

$$r = k_u c_{HSO_3^-}^{3/2} \quad (2)$$

where k_u is the uncatalyzed kinetic constant and c_{HSO3^-} the bisulfite ion concentration, with k_u = 1.19 x $10^{-4} m^{3/2}/mol^{1/2}s$ at a temperature T=45 °C.

Afterward, the reaction was carried out in the presence of a catalyst, in a laboratory-scale well-mixed reactor from [32], where the gas phase was a mixture of oxygen and nitrogen, while the liquid phase was obtained by mixing two aqueous solutions, one obtained by dissolving $Ca(OH)_2$ into a SO_2

solution and the other containing manganese sulfate [44]. The results have been interpreted following the approach indicated by Astarita et al. [47] that is, with increasing catalyst concentration, three different reaction regimes were identified, namely, the slow kinetic, the slow diffusional, and eventually the fast reaction regime, together with the transition from one regime to another. In particular, a parallel reaction mechanism was developed, according to which the overall reaction rate can be calculated as the sum of the uncatalyzed and catalyzed reaction rates, with the last being of first order in manganese ion, as expressed by the following equation:

$$r = k_u c_{HSO_3^-}^{3/2} + k_c c_{Mn^{2+}}, \quad (3)$$

where k_c is the catalyzed kinetic constant and c_{Mn2+} the bisulfite ion concentration, with k_c = 0.193 s^{-1} at T=45 °C.

In [42] results are reported from an experimental study of calcium bisulfite oxidation in the presence of catalysts (ferrous and manganese ions) both separately and simultaneously added in the reaction vessel of [32]. The experiments were performed at a fixed oxygen partial pressure (21.3 kPa) and at a temperature of 45 °C. The analysis of the experimental results, carried out by using the theory of mass transfer with chemical reaction, indicated that the slow reaction regime has been explored and the transition from the kinetic to the diffusional subregime identified. Experimental results as compared with those obtained in the presence of the single catalytic species (Mn^{2+} alone and Fe^{2+} alone) allowed one to observe the synergistic effect that the two catalysts added simultaneously have on the oxidation reaction.

In Figure 32, the behavior of the oxidation rate vs the bisulfite ion concentration is reported for each Fe^{2+} concentration level; evidently, the oxidation rate increases while the catalyst concentration increases in the range explored. Moreover, it can be seen that the oxidation rate grows while c_{HSO3-} increases until it reaches a plateau, where r becomes almost independent of it. To compare uncatalyzed and catalyzed experimental data, the kinetic equation previously found, Eq. (2), has been reported in the plot as a continuous line.

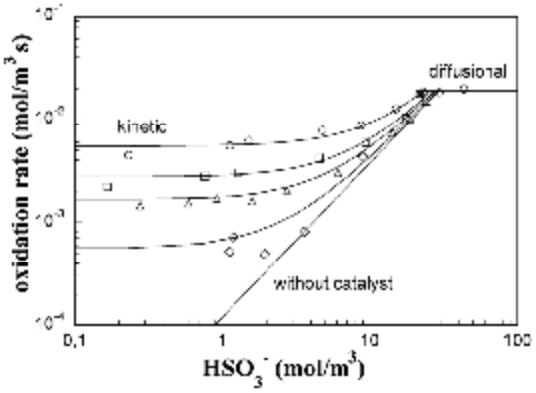


Fig. 32. Reaction rate as a function of c_{HSO3-} for four levels of c_{Fe2+}: ○- c_{Fe2+} = 0.010 mol/m^3; □- c_{Fe2+}= 0.005 mol/m^3; △- c_{Fe2+} =0.003 mol/m^3; ◇-, c_{Fe2+}=0.001 mol/m^3, [42, Fig. 2].

Figure 33 reports the behavior of the oxidation rate vs ferrous ion concentration. It can be noted that the oxidation rate increases with increasing c_{Fe2+}, until the upper limit of the diffusional ceiling is reached. Considering the uncatalyzed contribution, Eq (2), together with a ferrous-catalyzed contribution, the overall kinetic equation for ferrous-catalyzed bisulfite oxidation is

$$r = r_u + r_c = k_u c_{HSO_3^-}^{3/2} + k_c c_{Fe^{2+}} \quad (4)$$

where k_c is the constant of the catalyzed reaction, equal to 0.548 s^{-1}. The proposed reaction mechanism derives from testing of various kinetic models, among which this in-parallel model gives the best fit of the experimental data. Equation (4) is reported as a continuous line in Figures 32 and 33, showing that a quite good agreement with the experimental data in the kinetic subregime exists. Figure 34 shows the behavior of the oxidation rate as a function of the bisulfite concentration for a fixed Mn^{2+}/ Fe^{2+} ratio, equal to 4.1, obtained by varying the relative manganese and ferrous ion concentrations. It can be observed that the highest oxidation rate is reached at (e.g., c_{Fe2+} =0.008 mol/m^3 and c_{Mn2+} = 0.00328). The overall kinetic equation is thus

$$r = r_u + r_{c_1} + r_{c_2} = k_u c_{HSO_3^-}^{3/2} + k_{c_1} c_{Mn^{2+}} + k_{c_2} c_{Fe^{2+}} \quad (5)$$

where k_u is the kinetic constant of Eq. 2, k_{c1} is the rate constant of Eq. 3, and k_{c2} is the kinetic constant of Eq. (4). Equation (5) has been reported as a continuous line in Figure 34.

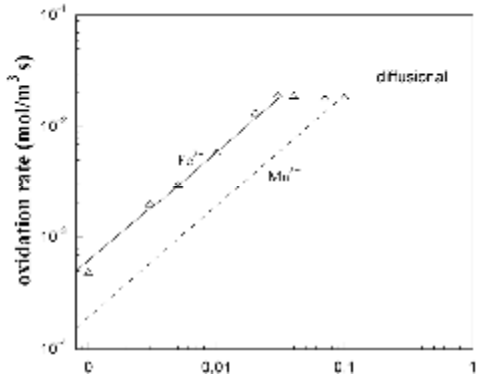


Fig. 33. Reaction rate as a function of the catalyst species concentration: △, Fe_{2+} concentration, [42, Fig. 3].

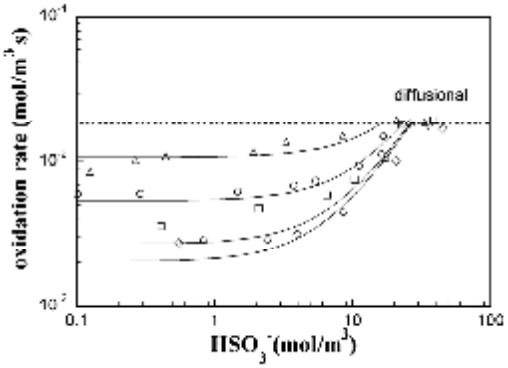


Fig. 34. Reaction rate as a function of c_{HSO3-} for c_{Mn2+}/c_{Fe2+} =4.1: Δ -c_{Mn2+}= 0.00328 mol/m^3 and c_{Fe2+} = 0.008 mol/m^3; ○-c_{Mn2+}= 0.0164 mol/m^3 and c_{Fe2+} = 0.004 mol/m^3; □-c_{Mn2+} = 0.0082 mol/m^3 and c_{Fe2+} = 0.002 mol/m^3; ◊-c_{Mn2+} = 0.006 15 mol/m^3 and c_{Fe2+}= 0.0015 mol/m^3, [42, Fig. 4].

The paper [43] deals with the experimental study of calcium bisulfite oxidation in the presence of catalysts (ferrous and cuprous ions). Experimental results have been compared with those obtained in the presence of the single catalytic species (Cu^+ alone and Fe^{2+} alone), showing that copper is less effective than iron as a catalyst; no synergy between the two catalysts added simultaneously has been observed.

5. CONCLUSION

The importance of the problem under consideration connected with preservation of air purity and on the other side the long term history of research and development in that area has resulted in a great amount of experimental information and technological solutions in the literature sources. The present work makes a review of the main principles and technological solutions and the studies from the last

years on wet FGD, the most widely used desulfurization technology. And yet at the present world level of 95% of SO_2 removal efficiency of this technology, the amount of SO_2 discharged in the atmosphere is huge. The aim of the present work is to help the finding of the proper direction of the efforts for new solutions and the choice of apparatuses and equipment.

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