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USE OF NATURAL SODA ASH PRODUCTION PROCESS WASTE FOR SO₂ REMOVAL

Results of ChemCad[®]6.0 simulation have been presented on usability of natural soda ash production process waste in order to remove SO₂ from flue gas. Properties and concentrations of the solutions used in this study belong to the waste stream of Eti Soda Inc., and the flue gas compositions were acquired from an existing thermal power plant. SO₂ and H₂O feed rates and flue gas entrance temperature to the absorption tower were optimized through the response surface methodology (RSM) in order to attain highest SO₂ removal yields. It has been found that SO₂ removal remained at 33.83% when the waste composition was lower than 2 wt. % while 100% SO₂ removal was reached as the waste composition was increased to 8 wt. %. This result clearly demonstrates that treatment of natural soda ash production process waste can be done safely and economically while serving as an SO₂ removal agent at the same time.

1. INTRODUCTION

World energy demand continuously grows up every passing day due to industrial and technological developments. New and renewable energy resources with more emphasis on fuel economy are needed to meet this growing demand without neglecting to establish better and efficient use of coal as the present and more abundant resource of energy. Lignites having high sulfur contents, when burned without preventive measures, produce sulfur dioxide (SO₂) which contributes most to the air pollution released to the atmosphere and causes many drawbacks for the living beings such as health problems and life quality [1]. Although 73% of the SO₂ emission originates from thermal power plants using fossil fuels and 20% comes from industrial systems, it is well known that household heating and transportation also contribute to elevated SO₂ levels in the atmosphere [2, 3]. It is unavoidable to have some obligations for the emission and removal of SO₂ originating from thermal power plants. Abiding the emission limits given in related regulations in terms of environmental pollution prevention policies as well as requirements of environmental technologies increase the importance of SO₂ removal from flue gas.

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Various procedures have been reclaimed to decrease SO₂ emission. Besides the primary techniques such as fuel enhancement and adsorption of SO₂ in the combustion chamber [4], there exist many different widely utilized secondary approaches to remove SO₂ from the flue gas by absorbing in wet and dry systems using ammonium, organic solvents and sea water as the sorbents [5, 6]. Current research on flue gas desulfurization by dry techniques has focused on new and original sorbents to control SO₂ emission [7, 8]. On the other hand, research on wet desulfurization techniques concentrated on design of absorption columns having higher capacities and better dehydrating performances with substantially lower pressure drops [9, 10] as well as on modeling studies using industrial desulfurization process data for validation [11]. Besides the reports on flue gas desulfurization using trona as the sorbent as well as evaluating its SO₂ absorption efficiencies and reaction mechanism, it is likely to come across some contributions assessing the effects of gas temperature, stoichiometric ratio and concentration of trona solution on SO₂ removal in spray dryers by comparing experimental data with modeling results [12]. On the other hand, process modelling, design and optimization using various simulation programs are frequently resorted to save time and resources [13–16]. Optimization of process operating conditions by the response surface methodology (RSM) has become a widely preferred approach in order to have a profound understanding on the main and interaction effects of factors on responses [17–19]. Response surface method has been used to optimize not only the experimental data but also the simulation results [20].

In this study, utilization of the waste stream of a process, producing Na₂CO₃ and NaHCO₃ from trona, in SO₂ removal from flue gas by wet techniques was investigated through ChemCad simulations. Among many other operating parameters, feed rate of SO₂, flue gas entrance temperature and sorbent feed rate were selected as independent parameters and their effects on SO₂ removal were identified by RSM approach using the central composite design (CCD).

Taking into account about 8% yearly increase in Turkey's energy demand of which almost 75% originates from thermal power plants, it is straight forward to comprehend that SO₂ removal by using the waste stream of natural soda ash process which itself requires an investment for disposal would be highly profitable. Additionally, this study concludes that SO₂ emission rates below the limits set by the environmental regulations for power plants of capacities between 100 and 300 MW using solid fuels are indeed attainable under the conditions tested.

2. EXPERIMENTAL

Sorbent solutions of compositions to be used in flue gas desulfurization were supplied by the Soda Ash and Sodium Bicarbonate Production Plant of Eti Soda Inc. located

in Beypazarı region of Ankara, Turkey. The solution was composed of a mixture of downstreams from monohydrate and decahydrate centrifuges of heavy soda (dehydrated Na₂CO₃) unit. The flow rate of the waste stream containing water, Na₂CO₃, NaHCO₃ (Table 1) was 50 m³/h. The waste was regularly stored in solution reservoirs or used in solution mining to push underground iron ore to the surface.

Table 1

Properties of natural soda ash production process waste

Parameter	Value
Temperature	20 °C
Density	1.3 g/cm ³
Concentration of Na ₂ CO ₃	3.056 mol/dm ³
Concentration of NaHCO ₃	0.321 mol/dm ³

Simulation studies were initiated with real process data regarding solution compositions and flow rates. However, ChemCad simulation software sets some limits for the sorbent flow rate based on the gaseous feed rate to the absorption tower. In other words, the sorbent flow rate was too high and resulted in divergence when the real process data were used for simulation. Therefore the flow rate of the sorbent stream was decreased by 10% without altering its composition. Furthermore, water content of the waste stream was insufficient to dissolve Na₂CO₃ and NaHCO₃ and some dilution was carried out according to solubility data of Na₂CO₃ and NaHCO₃ at 20 °C being 215 g/dm³ and 96 g/dm³, respectively. The calorific value and composition of lignite originating from a 150 MW power plant operating at 35% burning efficiency with 30% excess air are given in Table 2. Compositions of sorbent solution and flue gas fed to the absorption tower are given in Tables 3 and 4, respectively.

Table 2

Results of proximate and ultimate analysis of lignite used in the power plant [wt. %]

Component	Value
C	25.12
H	2.01
S	1.87
O	8.49
N	0.76
Ash	41.89
Humidity	19.86
Lower calorific value, kcal/kg	2248

Table 3

Composition of the waste sorbent solution
fed to the absorption column

Component	Flow rate [kmol/h]	Concentration [mol %]
Na ₂ CO ₃	15.283	0.320
NaHCO ₃	1.607	0.034
H ₂ O	4745	99.646

Table 4

Composition of the flue gas
fed to the absorption column

Component	Flow rate [kmol/h]	Concentration [mol %]
CO ₂	1023.59	11.31
SO ₂	28.06	0.31
N ₂	5727.97	63.29
H ₂ O	1919.58	21.21
O ₂	351.15	3.88
Total	9050.35	100.00

Simulation studies were carried out through wet desulfurization processes where CaCO₃, Na₂CO₃ and waste stream of natural soda ash production unit were used as the sorbents. In order to include chemical reactions, vapor-liquid equilibrium model was selected from the SCDS template for spray tower having neither a reboiler nor a condenser. As highly common in the industrial processes, sorbent stream was introduced from the top and the flue gas was introduced from the bottom of the absorption tower shown schematically in Fig. 1. Refined gas was released from the top of the tower while sulfite was drained from the bottom. SCDS is a multistage vapor-liquid equilibrium module which is able to compute single column calculations including distillation columns, absorbers and scrubbers. Basically, non-ideal distribution coefficients K are designed for the simulation of chemical systems. Derivative of each equation is calculated by the Newton–Raphson convergence method.

Optimum values of operating parameters for SO₂ removal process were determined by the response surface method based on the central composite design technique. Central composite design for three factors with 20 working points were applied in simulation studies. The SO₂ flow rate, flue gas entrance temperature and H₂O flow rate for the sorbent solution have been selected as the independent variables. The SO₂ removal efficiency was the response variable calculated based on the SO₂ contents of in and out flows to and from the absorption column using Eq. (1). Actual and coded levels of independent variables are listed in Table 5.

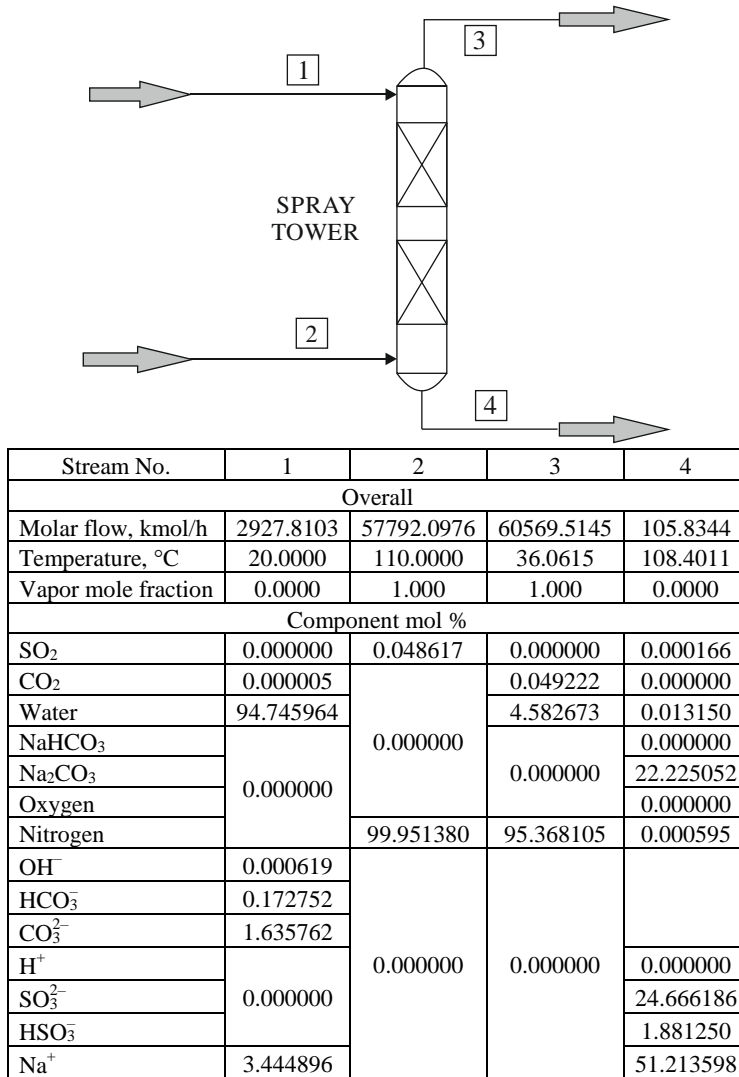


Fig. 1. Sample of absorption column model

$$R_{SO_2} = \frac{F_{SO_2} - F_{SO_{2out}}}{F_{SO_2}} \times 100 \tag{1}$$

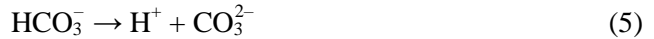
where R_{SO_2} is the removal efficiency of SO₂, %, F_{SO_2} – the flue gas (FG) inlet flow rate, kmol/h, $F_{SO_{2out}}$ – flue gas outlet flow rate, kmol/h.

Table 5

Actual and coded levels of the independent variables
used in the central composite design

Factor	-1	0	1	$-\alpha$	α
A F_{SO_2} , kmol/h	28.10	67.64	107.18	1.14	134.14
B T_{FG} , °C	50	80	110	29.55	130.45
C F_{H_2O} , kmol/h	3200	3972.50	4745	2673.32	5271.68

System components have been selected according to the sorbent used in the absorption tower. The electrolyte model was found to be appropriate to simulate absorption events which take place through ionization reactions and the Pitzer model was used for this purpose. Chemical reactions of the model are given as follows:



3. RESULTS

First of all effects of SO_2 content in the flue gas on removal efficiencies were tested using three different sorbent solutions in order to compare their SO_2 removal performances. Flue gas temperature and compositions of sorbent solution used for this purpose are given in Table 6. Figure 2 illustrates some reduction in SO_2 removal with an increase in SO_2 contents of the flue gas for all sorbent solutions. Flue gas entrance temperature is also an important parameter since it has profound effect on ionization and solution reactions in the absorption tower. Figure 3 presents the results of simulation performed at various temperatures of flue gas given in Table 7. As can be deduced from Fig. 3,

solutions containing CaCO₃ cannot be used for removal above 100 °C while Na₂CO₃ and waste sorbent solutions are still effective up to 160 °C.

Table 6

Flue gas (FG) inlet temperature and composition of the sorbent solution for the simulations examining the effects of SO₂ flow rate

T_{FG} [°C]	Sorbent solution	
	Component	Content [mol %]
40	CaCO ₃	1.87
	Na ₂ CO ₃	1.87
	waste	0.36

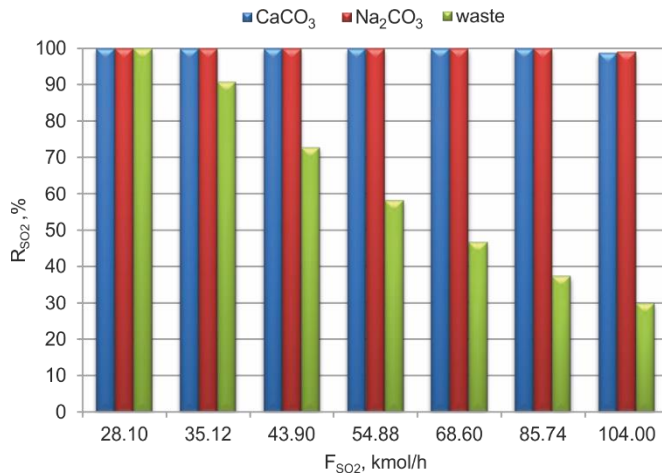
Fig. 2. Effect of SO₂ flow rate on SO₂ removal

Table 7

Flue gas SO₂ flow rate and composition of the sorbent solutions

F_{SO_2} [kmol/h]	Sorbent solution	
	Component	Content [mol %]
28.1	CaCO ₃	1.87
28.1	Na ₂ CO ₃	1.87
28.1	waste	0.36

Simulation results presented in Fig. 4 illustrate the effect of sorbent compositions on SO₂ removal when the SO₂ flow rate in flue gas was 28.1 kmol/h and flue gas temperature was 40 °C. According to these results, decrease in compositions of waste and Na₂CO₃ solutions in other words increase in H₂O flow rate lowers SO₂ removal severely.

Furthermore dilute solutions of waste and Na_2CO_3 show better performance compared to CaCO_3 solutions.

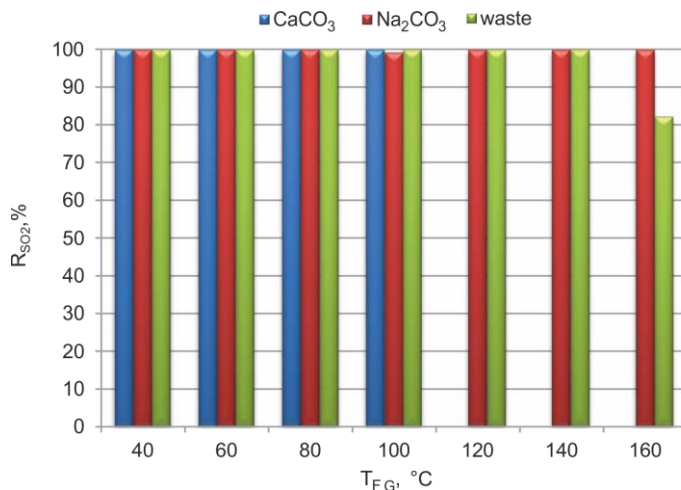


Fig. 3. Effect of flue gas temperature on SO₂ removal

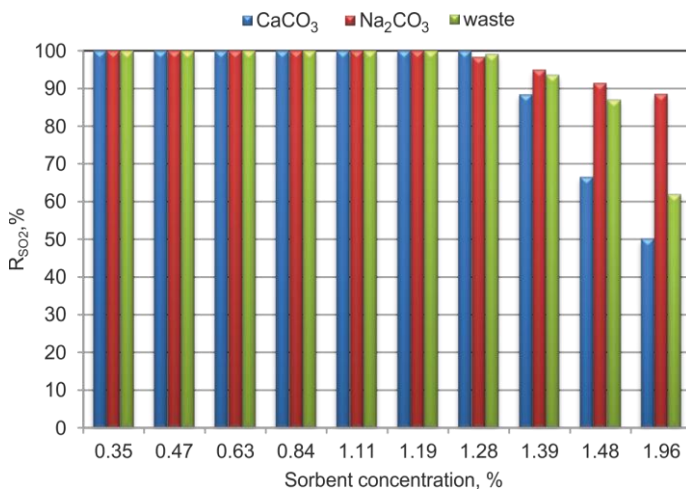


Fig. 4. Effect of sorbent concentration on SO₂ removal

Response values for SO₂ removal obtained at operating conditions given in Table 8 have been computed using Eq. (1). The regression coefficient, $\text{adj-}R^2$ and $\text{pred-}R^2$ values were calculated to be 0.8656, 0.84 and 0.774, respectively:

$$R_{\text{SO}_2}, \% = 102.57535 - 0.74173F_{\text{SO}_2} - 0.063055T_{\text{FG}} + 1.83584 \times 10^{-3}F_{\text{H}_2\text{O}} \quad (10)$$

Table 8

Operating points and their coded values for central composite design and the responses obtained from ChemCad simulations

Run	F_{SO_2} [kmol/h]		T_{FG} [°C]		F_{H_2O} [kmol/h]		R_{SO_2} [%]
1	0	67.64	0	80	0	3972.50	47.1332
2	1	107.18	-1	50	-1	3200	29.9769
3	0	67.64	0	80	0	3972.50	47.1332
4	α	134.14	0	80	0	3972.50	23.9235
5	0	67.64	0	80	0	3972.50	47.1332
6	0	67.64	0	80	$-\alpha$	2673.32	45.1633
7	0	67.64	0	80	0	3972.50	47.1332
8	-1	28.10	-1	50	-1	3200	100
9	0	67.64	0	80	α	5271.68	47.442
10	1	107.18	1	110	1	4745	29.7805
11	0	67.64	$-\alpha$	29.55	0	3972.50	47.6662
12	0	67.64	0	80	0	3972.50	47.1332
13	$-\alpha$	1.14	0	80	0	3972.50	100
14	-1	28.10	1	110	1	4745	100
15	-1	28.10	-1	50	1	4745	100
16	1	107.18	1	110	-1	3200	25.9639
17	0	67.64	α	130.45	0	3972.50	41.7763
18	1	107.18	-1	50	1	4745	30.1347
19	-1	28.10	1	110	-1	3200	88.4387
20	0	67.64	0	80	0	3972.50	47.1332

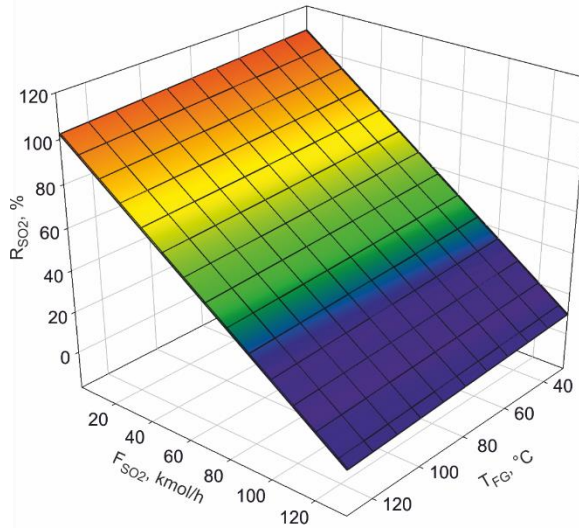


Fig. 5. Response surface representing the effects of F_{SO_2} and T_{FG} on SO_2 removal ($F_{H_2O} = 4745$ kmol/h)

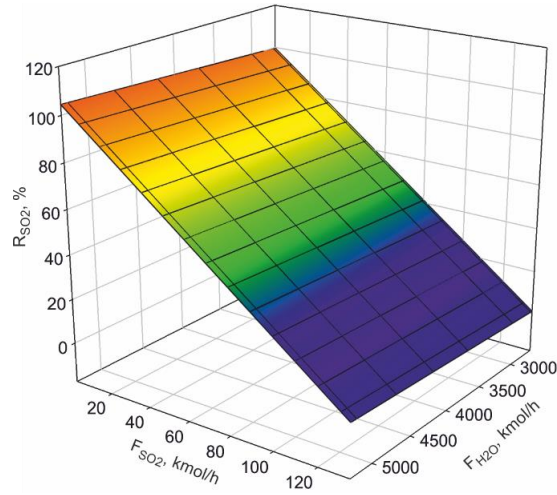


Fig. 6. Response surface representing the effects of F_{SO_2} and F_{H_2O} on SO_2 removal ($T_{FG} = 110\text{ }^\circ\text{C}$)

Response surface diagrams presented in Figs. 5 and 6 illustrate the effects of SO_2 content and temperature of the flue gas entering the absorption tower, on SO_2 removal. The figures (based on Eq. (10)) have been plotted for the maximum value of the third independent variable. Based on these results, the optimum values of independent variables yielding highest SO_2 have been determined as $F_{SO_2} = 28.10\text{ kmol/h}$, $T_{FG} = 50\text{ }^\circ\text{C}$ and $F_{H_2O} = 4745\text{ kmol/h}$.

Waste solutions of 2–10 wt. % have been tested to obtain higher SO_2 removal efficiencies and results are listed in Table 9. Simulation studies for SO_2 removal based on stoichiometrically calculated flue gas compositions of a 150 MW thermal power plant have shown that SO_2 content of the refined gas can be lowered below the limit value of 1300 mg/Nm^3 set by the environmental regulations by using the waste composition of 8 wt. %.

Table 9

SO_2 contents of the gas streams entering and leaving the absorption column and corresponding SO_2 removal yields for various waste compositions

$F_{Na_2CO_3}$ [kmol/h]	F_{NaHCO_3} [kmol/h]	F_{H_2O} [kmol/h]	Waste composition [wt. %]	F_{SO_2} [kmol/h]	$F_{SO_2,out}$ [kmol/h]	$F_{SO_2,out}$ [mg/Nm ³]	R_{SO_2} [%]
15.283	1.607	4745.00	2	93.99	62.19321	5464.61	33.83
19.104	2.009	4745.00	3	93.99	54.45699	4783.88	42.06
38.208	4.018	4745.00	5	93.99	17.36109	1524.62	81.53
45.849	4.8213	4745.00	6	93.99	3.304437	290.13	96.48
61.132	6.4284	4745.00	8	93.99	6.67E-13	5.86E-11	100.00
84.057	8.839	4745.00	10	93.99	7.52E-08	6.59E-06	100.00

4. CONCLUSIONS

Due to growing energy demands owing to industrial and technological developments, fossil fuels will continue to play important roles, as in the past, in order to attain sustainable progress with safe and reliable energy sources. Emerging desulfurization techniques and newly discovered sorbents will enable the use of fossil fuels having high sulfur contents in energy production. In this study, waste stream of a natural soda ash production process has been tested in terms of SO₂ removal from flue gas and demonstrated to be an alternative to widely used limestone. In addition, a waste stream which itself requires an extra cost and investment for elimination is shown to be disposed of in the same process.

ChemCad simulations were performed using waste solutions of 2 wt. % to evaluate the effects of SO₂ loading, flue gas temperature and H₂O feed rate on the SO₂ removal efficiency. Increase in SO₂ content of the flue gas resulted in decrease in the removal efficiency, and 100% removal was attained when maximum flow rate of SO₂ was 32 kmol/h. In terms of flue gas inlet temperature, 100% removal was attainable up to 140 °C but efficiencies decreased to 96.66 and 82.18%, respectively, as the inlet temperature of flue gas was raised to 150 °C and 160 °C. Reducing the H₂O content of the waste solution resulted in lower SO₂ removal efficiencies. Down to 1400 kmol/h H₂O feed rates, 100% removal was shown to be attainable depending on values of the other independent parameters.

The solution containing 2% waste with 15.283 kmol/h Na₂CO₃, 1.607 kmol/h NaHCO₃ and 4745 kmol/h H₂O flow rates was used as the sorbent and shown to result in 33.83% SO₂ removal. Solutions with higher waste contents were tested in order to increase removal efficiency and it was demonstrated that increasing the mass percent of the waste in the sorbent solution up to 8–10 wt. % results in 100% SO₂ removal while 6 wt. % waste solutions were just as effective to reduce the SO₂ content in the refined gas below the regulatory limits of 1300 mg/Nm³. It can be finally claimed that natural soda ash production process waste can be utilized in flue gas desulfurization. In order to attain required efficiencies of SO₂ removal, the capacity of the power plant and quality of the fuel have to be considered carefully to adjust the concentration of the waste solution entering the absorption tower.

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