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# Regeneration of Absorption Solutions Used In The Removal of Sulfur Dioxide From Gas Streams

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**Abstract**

*A bench scale system was built to study the regeneration of sodium hydroxide used for then absorption of sulfur dioxide by reaction with lime suspension. The method of Box-Wilson experimental design was employed for the determination of the optimum conditions which give the highest regeneration efficiency. The optimum conditions of sodium hydroxide regeneration reaction were:*

*feed ratio 0.59,*
*reaction temperature of 14°C*
*reaction time of 31 min.*

*These correspond to the maximum regeneration efficiency of 95%.*

## إستعادة محاليل الامتصاص المستعملة لازالة ثنائي أوكسيد الكبريت من المخرجات الغازية لمصنع حامض الكبريتيك

**الخلاصة**

بعد عملية امتصاص غاز $SO_2$ بواسطة محلول هيدروكسيد الصوديوم تمت استعادة هيدروكسيد الصوديوم المستهلك بواسطة تفاعل ناتج الامتصاص (كبريتيت الصوديوم) مع هيدروكسيد الكالسيوم. تم في هذا البحث إستخدام منظومة مختبرية لدراسة تأثير نسبة كبريتيت الصوديوم إلى هيدروكسيد الكالسيوم (٠،٠٥ - ٢٥ر١)، درجة حرارة التفاعل (١٠ - ١٥ م) وزمن التفاعل (٥ - ٤٠ دقيقة) باستخدام طريقة BOX-WILSON في تصميم تجارب الاستعادة.

لقد تم تعيين الظروف التشغيلية المثلى التي تحقق أقصى إنتاجية لهيدروكسيد الصوديوم وهي: نسبة كبريتيت الصوديوم الى هيدروكسيد الكالسيوم (٠،٥٨٩)، درجة

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حرارة التفاعل (١٤ م) زمن التفاعل (٣١ دقيقة ). وكانت كفاءة الاستعادة عند الظروف المثلى (٩٥ %)، وتم تمثيل هذه العلاقة بشكل ناجح بمعادلة سطح من الدرجة الثانية.

## INTRODUCTION

The removal of sulfur dioxide from a gas stream can be done by either adsorption on some active solid [1], catalytic oxidation and separation by cooling [2] and absorption by various solutions such as water, ammonia, sodium hydroxide and lime [3]. Among the new approaches is the dry process in which calcium hydroxide is injected in the duct system followed by the separation of the solid particles coming up with the flue gas stream [4]. Recently, cyclic activation of $Ca(OH)_2$ was introduced by Krammer et al [5] through the withdrawal of the sorbent from the flue gas and its re-injection up-streams in the duct to enhance the solid conversion by increasing the residence time.

The double alkali process [6] involves the use of one alkali (sodium hydroxide) to scrub the sulfur dioxide from the flue gas, and another alkali to regenerate the initial alkali, and to precipitate calcium sulfite [7], which is separated and sent to waste as dewatered solid:

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O \quad (1)$$

$$Na_2SO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_3 \quad (2)$$

The details were not published for double alkali process as regard to pilot plant operation and remained as the property of the licensing companies. Parkinson [8] demonstrated sulfur dioxide removal techniques and reported the 30-40 double alkali systems have been installed world-wide by 1982. The process facility was operable 93% of the time over a one-year period and average SO2 removal of 92% compared with about 73% operability and 80-90% sulfur dioxide removal for limestone systems. Richard [9] reported that limestone is sold for 1/4 the cost of lime but contains only one-half as much calcium by weight as a regeneration reagent and long time is needed for the regeneration [10].

In this paper a study was carried out to evaluate the optimum conditions for the regeneration of sodium hydroxide used in the absorption of sulfur dioxide by reacting the produced sodium sulfite solution with calcium hydroxide employing Box-Wilson method of experimental design.

## EXPERIMENTAL

### Regeneration system:

In a round bottom flask, 250 ml of $Ca(OH)_2$ slurry (containing 50 g) was placed. The flask was maintained at the desired temperature using a water bath and connected to a dropping funnel to deliver the sodium sulfite solution (250ml). At the end of each experiment, the reaction products were filtered. The filtrate was titrated vs. standard HCl solution to estimate the quantity of NaOH produced. The system is schematically shown in Fig. 1. The generation of $SO_2$ and absorption were performed in accordance with recent reports [6,11].

### Chemicals:

All chemicals and reagents were of analytical grade. Distilled water was used for the preparation of working solutions and washing of the glassware.

### Results And Discussion

Box - Wilson orthogonal central composite design was used to conduct the experiments. Three variables were considered:

feed ratio ($Na_2SO_3$ : $Ca(OH)_2$) of 0.05 to 1.25;

reaction time of 5 to 40 min;

and reaction temperature of 10 to 50° C.

The actual values of the three variables used in each experiment are calculated by rearranging the coding conversion [12] as given in Table 1. The results of the response (regeneration efficiency) of the experiments conducted according to box - Wilson method are also listed in Table 1. The coded data of Table 1 was fitted to the quadratic (second degree) multi-variable polynomial [13] to get the correlation equation:

$$Y = 86.3560716 - 3.9031167 X_1 - 5.8291468 X_2 + 9.9401379 X_3 - 10.7793089 X_1^2 - 2.0531303 X_2^2 - 5.6181728 X_3^2 + 0.000125 X_1X_2 - 0.000125 X_1X_3 + 0.000125 X_2X_3 \quad (3)$$

$R = 0.9984$, $s = 1.42\%$

To test the significance of each term in equation (3 ), the F-distribution test was used employing the variance of each term in multi-variable correlation [17]. The results of calculations are listed in Table 2, where each computed F-value is compared with the critical F-value and □ was chosen to be 0.05 (95% confidence) with (n-j-1) = 5 to give Fa(1,5)=6.61 [14].

According to Table 2, the terms of interaction between variables ($X_1X_2$, $X_1X_3$ and $X_2X_3$) are insignificant. Thus, it is clear that the best form of equation (3) is

$$Y= 86.3560716 - 3.9031167\, X_1 -5.8291468\, X_2 + 9.9401379\, X_3 - 10.7793089\, X_1^2 - 2.0531303\, X_2^2 - 5.6181728\, X_3^2 \quad (4)$$

To generate a more useful equation for the regeneration reaction efficiency, the actual data of Table 2 are fitted to the quadratic (second degree) multi-variable polynomial [16]. The equation is

$$Y = 6.8602065 - 105.458757\, X_1 - 0.4324854\, X_2 + 3.4568255\, X_3 - 89.7539883\, X_1^2 - 0.0154935\, X_2^2 - 0.0549517\, X_3^2 \quad (5)$$

$R = 0.9987$ , $s = 1.018\%$

The maximum regeneration efficiency was evaluated by differentiating the fitted polynomial equation (5) with respect to each independent variable separately, and equating the derivatives to zero. When these three equations are solved, values of $X_1$, $X_2$ and $X_3$ corresponding to the maximum regeneration efficiency % ($y_{max}$.) can be found 0.588, 13.95°, 31.45 min. and 95.225%, respectively.

**Effect of Feed Ratio**

Figures 2 and 3 show the effect of feed ratio on regeneration efficiency (E%) at different reaction time intervals and temperature, respectively. The (E%) increased with increasing the feed ratio from 0.05 to 0.588, where maximum E% was attained. The E% decreased afterwards with increasing the feed ratio. Such a behavior is attributed to the variation of activity coefficients of the ions in the reaction mixture with concentration. Calcium hydroxide is a sparingly soluble species in water and the activity coefficient of the OH-ion is almost constant regardless of the percentage of the material in the suspension. On the other hand, the activity of SO3= ion decreases beyond the optimum value 0.588. Thus, the ratio $([OH^-]^2/[SO_3^=])$ decreases with the increase of $SO_3^=$ concentration and hence lower rate will be expected for the regeneration reaction, as explained by Charles at al [7] and Weast [15], which lowers the degree of conversion or the E%.

However, $CaSO_3$ production is controlled by the ionic product $[Ca^2+][SO_3=]$ and the initial pH when a soluble salt such as CaCl2 is taken as the source of calcium [16].

**Effect of Reaction Temperature**

The effect of reaction temperature on the regeneration efficiency is shown in Figs. (4) and (5). These figures indicate that at higher temperatures larger feed ratio and longer reaction time are necessary to obtain reasonable values of regeneration efficiency. The reason of this reaction temperature behavior is that the activity coefficient of $SO_3^{2-}$ decreases with temperature [15], while that of $OH^-$ is constant with temperature. Thus, the equilibrium ratio $([OH]/[SO_3])$ will decrease with increasing in the temperature [17], or in other words, the regeneration efficiency decreases.

On thermodynamic basis, Gibbs free energy of the reaction goes to more positive values with increasing the temperature. Furthermore, the exothermic nature of the reaction ($\Delta H^\circ$ = -2.535 kJ. .g $mol^{-1}$) makes it more favorable at lower temperatures in accordance with Le Chateleir principle.

**Effect of Reaction Time**

Figs. 6 and 7 show the effect of reaction time on the regeneration is clear that the efficiency increased with increasing reaction time from 5 to 31.45 min., beyond this time the efficiency decreased slightly. Partial hydrolysis of the calcium sulfite formed account to this slight decrease in regeneration efficiency in accordance with chemical reaction equilibrium principle, as explained by Charles et al. [7].

Figs. 6 and 7 show that there is no interaction between feed ratio and reaction temperature, feed ratio and reaction time, and reaction temperature and reaction time, respectively.

**Effect of sodium sulfate**

Among the possible constituents of the gaseous products of the sulfuric acid plants is the sulfur trioxide as a result of incomplete absorption in sulfuric acid. The absorption of this $SO_3$ in sodium hydroxide results in the formation of sodium sulfate. Thus, it was necessary to investigate the effect of sodium sulfate on the regeneration of NaOH from sodium sulfite. Two additional experiments were conducted at the optimum conditions where $Na_2SO_4$ was incorporated in $Na_2SO_3$ feed solution.

As shown in Table 3, the presence of sodium sulfate in the reaction mixture upon the regeneration efficiency is insignificant (only 0.33%). The same conclusion was reported by Charles et al [7]. This is due to the fact that sodium sulfate is an inert material as explained by Rosenberg et al [18].

**Effect of Calcium sulfite**

Two additional experiments (1 and 1C) were conducted to study the effect of the existence of calcium sulfite (the main by-product of the regeneration reaction) on the efficiency of the process. The dried solid product of the regeneration was incorporated in the reaction mixture together with new lime. The results are given in Table 4. The efficiency sharply decreased (33.66%), when $CaSO_3$ was present in the mixture. The calcium sulfite (as a product) accelerates the reaction to reach the chemical equilibrium state as explained by Charles et al. [7]. Thus the solid product, of the regeneration reaction cannot be recycled directly to the next batch and washing/filtration step is required to purify $Ca(OH)_2$ from $CaSO_3$ as suggested by many authors [19, 20].

**Reaction Kinetics**

The kinetics of the regeneration of sodium hydroxide from sodium sulfite was studied to find the order and the rate constant of the reaction to fulfill the necessary data for the reactor design. The experimental data are given in Table 5. Three relationships are examined:

1$^{st}$ order with respect to sodium sulfite I;

2$^{nd}$ order with respect to sodium sulfite II

and 2$^{nd}$ order ( both calcium hydroxide and sodium sulfite III).

However, the second order relation type II gave the best linearity and passing through the origin (Fig. 8). This confirms the results reported elsewhere [7, 21]. According to the integrated rate equation of the second order reaction, the rate constant was evaluated to be 0.45 $L.gmol^{-1}.min^{-1}$ at 40 °C.

## CONCLUSIONS

Sodium hydroxide used in the absorption of sulfur dioxide from the gases of sulfuric acid plant can be regenerated efficiently by the reaction with lime slurry. The optimum conditions for the regeneration are feed ratio ($Na_2SO_3$ weight to $Ca(OH)_2$ weight) of 0.588, 14 °C and reaction time of 31.5 min. However, calcium sulfite which is the main by-product severely lowers the rate of the regeneration reaction and hence, the reaction effluent must be treated prior to the recycling of excess lime to the new batch.

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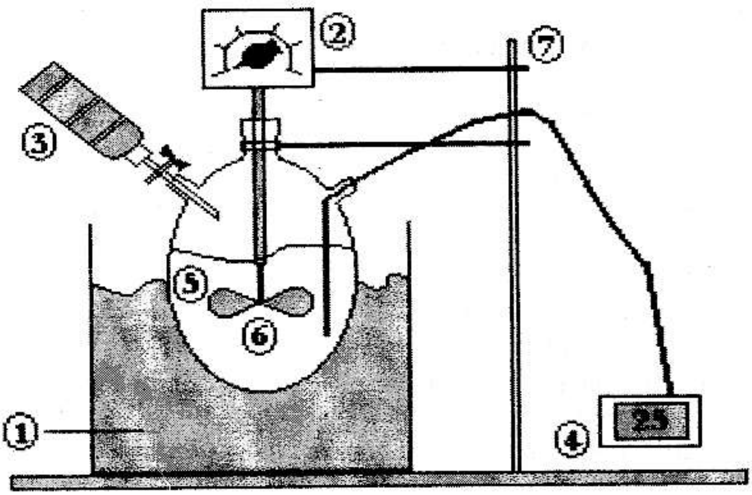


**Figure 1. Schematic Diagram Of The Regeneration System.**
**1, Water bath; 2, Stirrer controller; 3, Dropping funnel; 4, Digital thermometer; 5, Reaction flask; 6, Stirrer and 7, Stand**

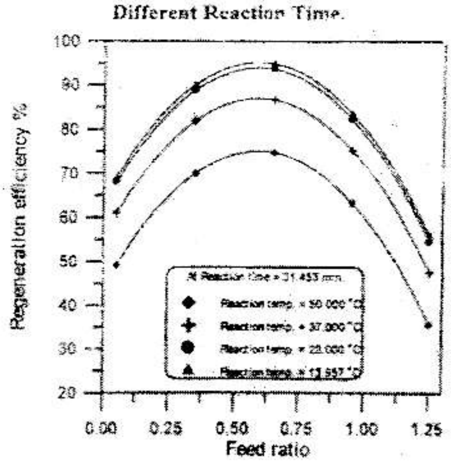


FIG.2: THE EFFECT OF FEED RATIO ON REGENERATION EFFICIENCY % AT DIFFERENT REACTION TIME

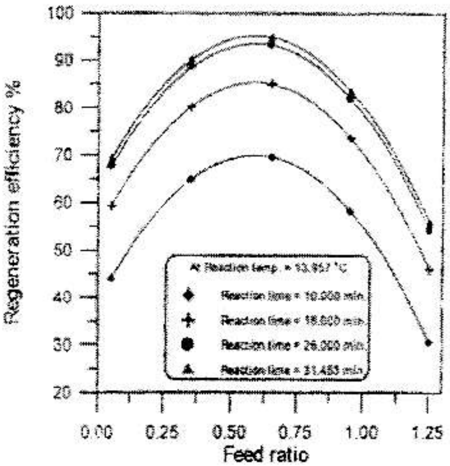


FIG.3: THE EFFECT OF FEED RATIO ON REGENERATION EFFICIENCY % AT DIFFERENT REACTION TEMPERATURE

**Efficiency % at Different Feed Ratio.**

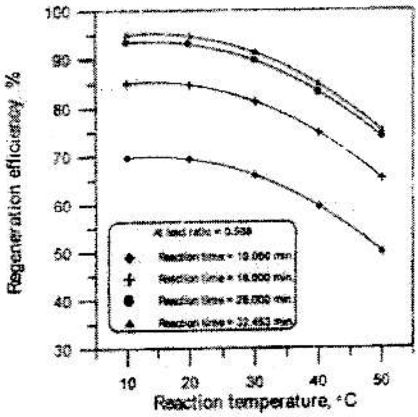


**FIG.4: THE EFFECT OF REACTION TEMPERATURE ON REGENERATION EFFICIENCY % AT DIFFERENT FEED RATIO**

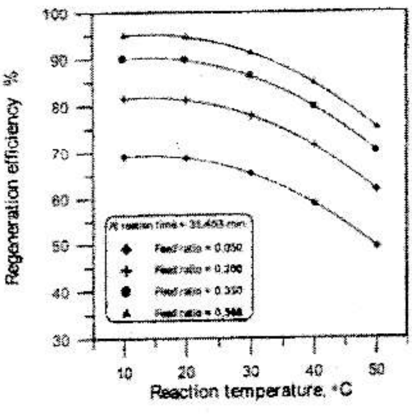


**FIG.5: THE EFFECT OF REACTION TEMPERATURE ON REGENERATION EFFICIENCY % AT DIFFERENT REACTION TIME**

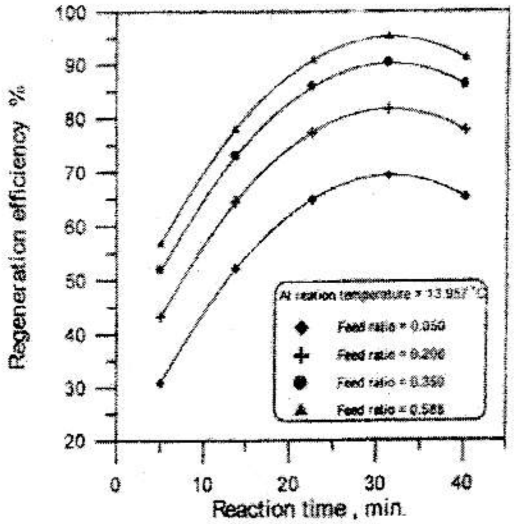


**FIG.6: THE EFFECT OF REACTION TIME ON REGENERATION EFFICIENCY % AT DIFFERENT FEED RATIO**

**at Differant Feed Ratio.**

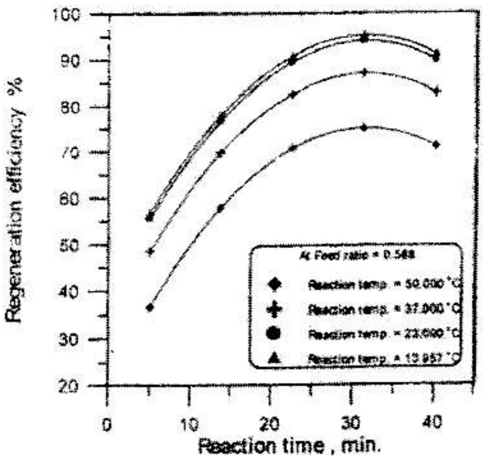


**FIG.7: THE EFFECT OF REACTION TIME ON REGENERATION EFFICIENCY % AT DIFFERENT REACTION TEMPERATURE**

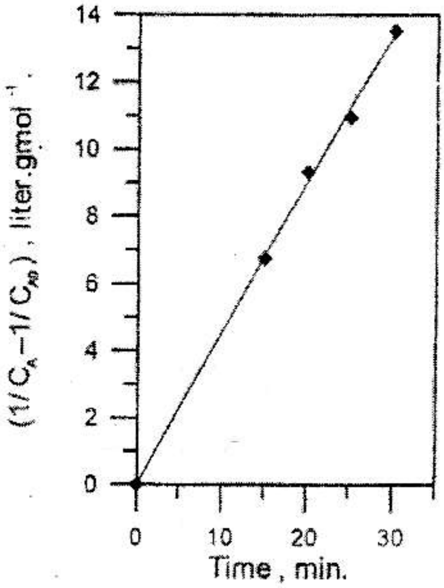


**FIG.8 SECOND ORDER REACTION TEST (WITH RESPECT TO $Na_2SO_3$ ONLY)**

Table 1 . The Experimental Results According To Box -Wilson Method

| Run No. | Actual Variables | | | Coded Variables | | | esponse Y% |
|---|---|---|---|---|---|---|---|
| | X1 | X2 | X3 | X1 | X2 | X3 | |
| 1 | 0.304 | 19 | 12.4 | -1 | -1 | -1 | 67.784 |
| 2 | 0.997 | 19 | 12.4 | 1 | -1 | -1 | 59.993 |
| 3 | 0.304 | 42 | 12.4 | -1 | 1 | 1 | 54.894 |
| 4 | 0.997 | 42 | 12.4 | 1 | 1 | -1- | 47.102 |
| 5 | 0.304 | 19 | 32.6 | -1 | -1 | 1 | 88.403 |
| 6 | 0.997 | 19 | 32.6 | 1 | -1 | 1 | 80.612 |
| 7 | 0.304 | 42 | 32.6 | -1 | 1 | 1 | 75.513 |
| 8 | 0.997 | 42 | 32.6 | 1 | 1 | 1 | 67.722 |
| 9 | 0.050 | 30 | 22.5 | -1.0732 | 0 | 0 | 61.001 |
| 10 | 1.250 | 30 | 22.5 | 1.732 | 0 | 0 | 47.464 |
| 11 | 0.650 | 10 | 22.5 | 0 | -1.732 | 0 | 89.074 |
| 12 | 0.650 | 50 | 22.5 | 0 | 1.732 | 0 | 71.727 |
| 13 | 0.650 | 30 | 5.0 | 0 | 0 | -1.732 | 53.343 |
| 14 | 0.650 | 30 | 40.0 | 0 | 0 | 1.732 | 86.069 |
| 15 | 0.650 | 30 | 22.5 | 0 | 0 | 0 | 86.356 |

Table 2. Analysis Of Variance For Orthogonal Variables

| Sum of Squares | Degree of Freedom | Mean Square | Computed F | | Conclusion |
|---|---|---|---|---|---|
| $X_1$ | 213.268 | 1 | 213.268 | 105.945 | S |
| $X_2$ | 475.681 | 1 | 475.681 | 236.304 | S |
| $X_3$ | 1383.211 | 1 | 1383.211 | 687.139 | S |
| $X_1^2$ | 28936.335 | 1 | 28936.355 | 14374.742 | S |
| $X_2^2$ | 40364.309 | 1 | 40364.309 | 20051.818 | S |
| $X_3^2$ | 35466.164 | 1 | 35466.164 | 17618.561 | S |
| $X_1X_2$ | $0.125*10^{-6}$ | 1 | $0.125*10^{-6}$ | $6.21*10^{-8}$ | NS |
| $X_1X_3$ | $0.125*10^{-6}$ | 1 | $0.125*10^{-6}$ | $6.21*10^{-8}$ | NS |
| $X_2X_3$ | $0.125*10^{-6}$ | 1 | $0.125*10^{-6}$ | $6.21*10^{-8}$ | NS |
| Error | 10.067 | 5 | 2.013 | | |

Table 3 Regeneration Efficiency With and Without $Na_2so_4$ .

| Run No. | Feed Ratio ($gNa_2SO_3/gCa(OH)_2$ | Temp, °C | Time, min. | Regeneration Efficiency % |
|---|---|---|---|---|
| 1 | 0.65 | 40 | 20 | 77.91 |
| 1N | 0.65 | 40 | 20 | 78.24 |

Table 4 Regeneration Efficiency With And Without $Caso_3$.

| Run No. | Feed Ratio ($gNa_2SO_3/gCa(OH)_2$ | Temp, °C | Time, min. | Regeneration Efficiency % |
|---|---|---|---|---|
| 1 | 0.65 | 40 | 20 | 77.91 |
| 1N | 0.65 | 40 | 20 | 44.25 |

Table 5: Time And Concentration Data For Sodium Sulfite And Calcium Hydroxide During Regeneration Reaction

| Time min. | $C_A$ gmol.L $^{-1}$ | $C_B$ gmol.L $^{-1}$ |
|---|---|---|
| 0 | 0.394 | 1.351 |
| 15 | 0.108 | 1.065 |
| 20 | 0.084 | 1.041 |
| 25 | 0.074 | 1.031 |
| 30 | 0.062 | 1.019 |