

TARIQ A. MAHMOUND*, BOHDAN J. GŁOWIAK, ANDRZEJ KUKLIŃSKI**

CALCULATION OF POLLUTION DOSE VARIATIONS DUE TO THE CONVERSION OF SO_2 TO H_2SO_4

Pasquill's formula is used to determine the variations occurring in the structure of the emission field due to the conversion of SO_2 to the aerosol of H_2SO_4 in the atmosphere. It is found that the conversion process exerts a considerable effect on the total pollution rate. The calculation method suggested permits the determination of the most hazardous conditions under which a maximum pollution dose occurs due to the simultaneous occurrence of SO_2 and H_2SO_4 .

1. INTRODUCTION

Sulphur dioxide and its oxidation products are ranked among the most common and widespread air pollutants. Most studies are concerned with the properties of SO_2 and the magnitude of SO_2 environmental concentrations. Yet, the number of literature reports on the oxidation rate of SO_2 in air is rather scarce. SO_2 may be removed from the atmosphere by photochemical oxidation in the gas phase and by catalytic oxidation in fog droplets. Thus, the gaseous particles of SO_2 are converted into aerosols containing sulphate-ions.

It was found that heterogeneous reactions of SO_2 in the atmosphere with suspended particulate matter proceeded faster than homogeneous ones. There is substantial evidence [1] that in the presence of powdered oxides of aluminium, calcium, chromium, iron, lead, and vanadium SO_2 reacted within minutes without sunlight or UV irradiation.

Many studies are reported on the catalytic activity of metals and on the reactions that take place at varying pH of the solution. Numerous mechanisms are suggested for the oxidation of sulphite ions to sulphates; most often, however, a radical mechanism of the oxidation reaction is being accepted, especially in the study of the SO_2 oxidation in solution and its role in the atmospheric chemistry [2].

* Environmental Engineering, University of Mosul, Iraq.

** Institute of Environment Protection Engineering, Wrocław Technical University, Wrocław, Poland.

The effect of iron on the oxidation of sulphate ions was investigated under conditions similar to the real ones [1]. The studies have revealed that not only sulphite ions but also HSO_3^- ions (i.e., SO_2 dissolved in the water) and non-dissociated particles may be readily oxidized. The reaction rate was found to be strongly pH-dependent, and was the highest when the pH of the solution fell in the range 5.2–7.

The catalytic oxidation of SO_2 in solution is, however, first of all affected by air humidity. It was observed that with increasing relative humidity (RH) the oxidation rate increased rapidly when RH ranged from 80 to 90%, the oxidation rate exceeded 8 times that observed at lower RH values, being 64 times higher at 80–95% RH.

Generally, it is expected that the SO_2 oxidation rate will increase with increasing temperature, however, some physical-chemical processes occur which will decrease the oxidation efficiency when the temperature increases.

It has been noted [4] that some of the dust particles suspended in Tokyo air were capable of generating sulphuric acid particles, while other airborne particles were not able to do so. Another report [3] presents the results of laboratory experiments in a closed chamber, which show that the percent of SO_2 conversion is higher when airborne particulate matter is present.

2. CALCULATION PROCEDURE

Considering certain difficulties that appear when determining the SO_2 to H_2SO_4 conversion, a method is suggested which permits a determination of the emission field structure variations caused by the conversion of SO_2 to SO_3 and next to the aerosol of H_2SO_4 .

The calculations of SO_2 and H_2SO_4 concentrations in the atmosphere are based on the conventional Pasquill's formula [5]:

$$S = \frac{E}{\pi \bar{u} \sigma_y \sigma_z} \exp\left(-\frac{H^2}{2\sigma_z^2}\right)$$

where E — the mass rate of emission (mg/s), σ_y — coefficient of atmospheric diffusion in the direction y (m), σ_z — the coefficient of atmospheric diffusion in the direction z (m), \bar{u} — arithmetic mean of wind speed for the air layer between the ground level and the effective height of the pollution dose (m/s), and H — the effective height of the emission source (m).

Assuming an arbitrary degree of SO_2 conversion, the following calculations were performed.

(1) The concentration of convertible SO_2 using the formula

$$C_{\text{SO}_2} = S \cdot \exp\left(-\frac{0,693 \tau}{\tau_{1/2}}\right).$$

(2) The concentration of H_2SO_4 generated in the conversion process by means of the formula

$$C_{\text{H}_2\text{SO}_4} = 1.5 S \left[1 - \exp \left(- \frac{0,693 \tau}{\tau_{1/2}} \right) \right]$$

where τ indicates the residence time in the atmosphere ($\tau = x/\bar{u}$); 1.5 is the stoichiometric coefficient for the conversion of SO_2 to H_2SO_4 ; $\tau_{1/2}$ stands for the half-time of SO_2 conversion, and x represents the distance from the measuring point to the emission source along the wind direction.

(3) The emission dose from equation

$$D = C_{\text{SO}_2} + C_{\text{H}_2\text{SO}_4} K$$

where K is the ratio of admissible SO_2 to admissible H_2SO_4 , whence

$$D = C_{\text{SO}_2} + 3 C_{\text{H}_2\text{SO}_4}.$$

To verify the procedure assumed, SO_2 and H_2SO_4 concentrations have been calculated for a copper smelter emitting SO_2 together with metal-containing dusts which increase the conversion rate. The amounts of SO_2 emitted reach 484 g/s, and the geometrical height of the emitter is 150 m. The calculations of SO_2 and H_2SO_4 concentrations were carried out for a critical wind speed (u_1) of 1 m/s (the effective height of the emission source is 188 m) and the equilibrium states C and D . The SO_2 to H_2SO_4 conversion was considered as a function of the half-life of SO_2 ($\tau_{1/2}$). The accepted $\tau_{1/2}$ -value ranged from 20 min to 5h, which corresponds to the conversion rate varying from about 0.2 %/min to 35 %/min. The results are presented in fig. 1-3.

From fig. 1 it is easily seen that the variations in SO_2 concentrations are the highest at $\tau_{1/2} = 20$ min. The same is true for the concentrations of the generated H_2SO_4 . The maximum SO_2 concentration is then reduced from 1.7812 mg/m³ to 1.4076 mg/m³. At the assumed half-life time ($\tau_{1/2} = 20$ min) the maximum SO_2 concentrations appear at a distance (x) from the emission source, which in this case is smaller than that when no conversion takes place ($x = 500$ m and 600 m, respectively).

Maximum concentrations of the generated H_2SO_4 reach 0.5608 mg/m³ (for $\tau_{1/2} = 20$ min) and appear at a distance of about 700 m. The gradient of H_2SO_4 concentrations is lower than that of SO_2 concentrations, because at a distance of some 1400 m from the emission source the concentration of H_2SO_4 continues to increase and prevails over SO_2 present in the atmosphere.

It is evident that the pollution dose increases rapidly with conversion rate (fig. 4): from 1.8781 mg/m³ at $\tau_0 = 5$ h up to 3.0888 mg/m³ at $\tau_{1/2} = 20$ min! From fig. 2 it is readily observed that at a wind speed (u) of 3.2 m/s the pollution radius is also significantly increased. At long distances from the emission source H_2SO_4 concentrations exceed the original concentration of SO_2 . The maximum concentration value of the generated H_2SO_4 is 0.1495 mg/m³ (for $\tau_{1/2} = 20$ min) and approaches half that of SO_2 .

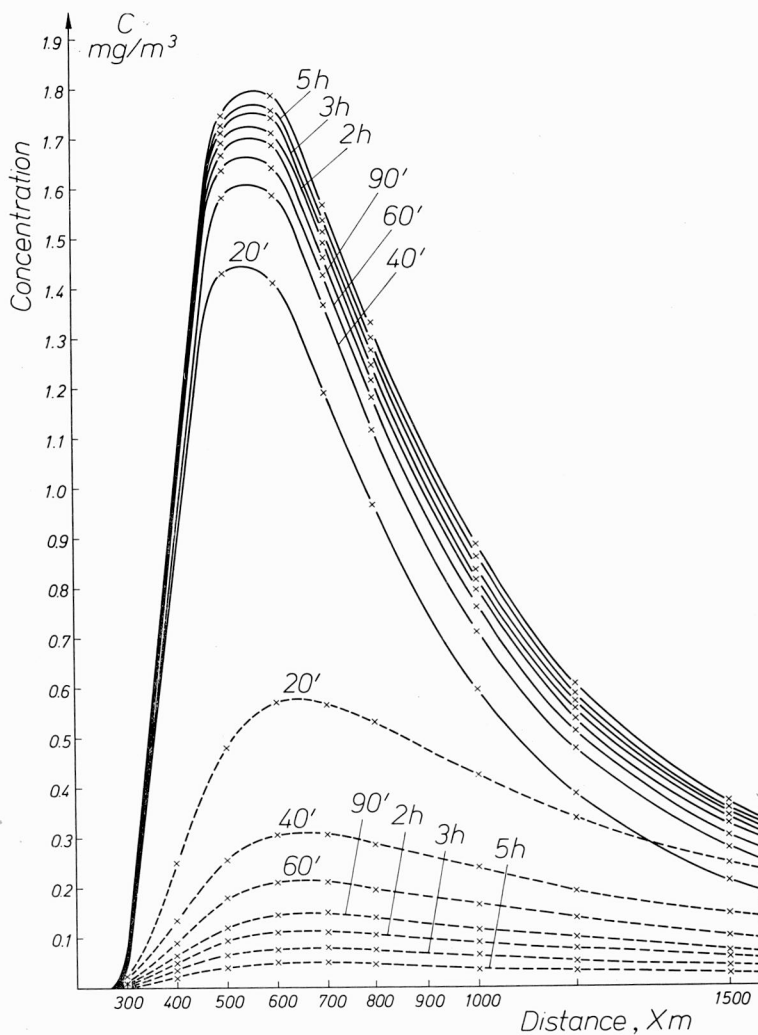


Fig. 1. Atmospheric diffusion of SO_2 and H_2SO_4 ($\tau_{1/2}$, equilibrium state A, $\bar{u} = 1.0$ m/s)

— CSO_2 , --- CH_2SO_4

Rys. 1. Rozkład stężeń SO_2 i H_2SO_4 przy założeniu konwersji dla różnych wartości $\tau_{1/2}$, stan równowagi A, $\bar{u} = 1,0$ m/s

— CSO_2 , --- CH_2SO_4

For the atmospheric equilibrium state D (fig. 3), H_2SO_4 concentrations are found to be higher than those for the equilibrium state C — although the initial SO_2 concentrations were lower. The maximum concentration of H_2SO_4 is 0.1957 mg/m^3 ($\tau_{1/2} = 20$ min). At higher wind speeds the SO_2 pollution radius decreases rapidly and the pollution radius of H_2SO_4 increases.

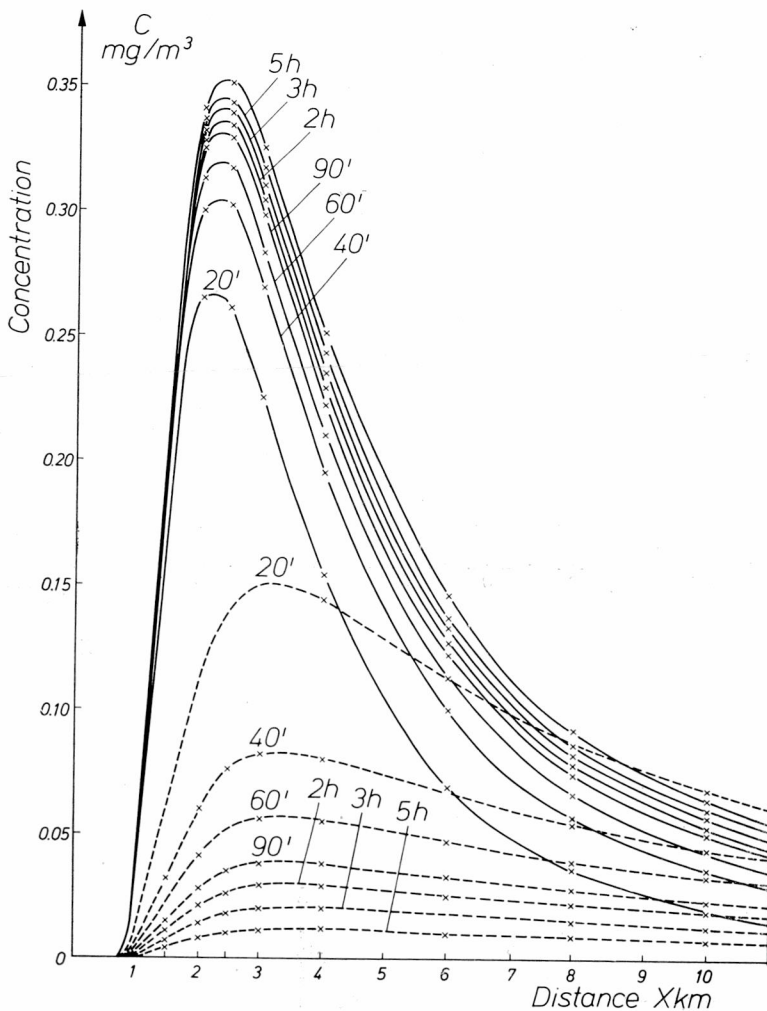


Fig. 2. Atmospheric diffusion of SO_2 and H_2SO_4 ($\tau_{1/2}$, equilibrium state C , $\bar{u} = 3.2$ m/s)

— C_{SO_2} , --- CH_2SO_4

Rys. 2. Rozkład stężeń SO_2 i H_2SO_4 przy założeniu konwersji dla różnych wartości $\tau_{1/2}$, stan równowagi C , $\bar{u} = 3,2$ m/s

— C_{SO_2} , --- CH_2SO_4

Fig. 4 represents pollution dose variations as a function of weather conditions. These variations are indicated by the increase of concentrations from 0.3752 to 0.6743 mg/m^3 (at $x = 2500$ m) and from 0.2818 to 0.6822 mg/cm^3 (at $x = 6000$ m) for the equilibrium states C and D , respectively.

The results of our studies show that the conversion process yields considerable amounts of H_2SO_4 which contribute to the total pollution rate. For $\tau_{1/2}$ ranging between 20 min

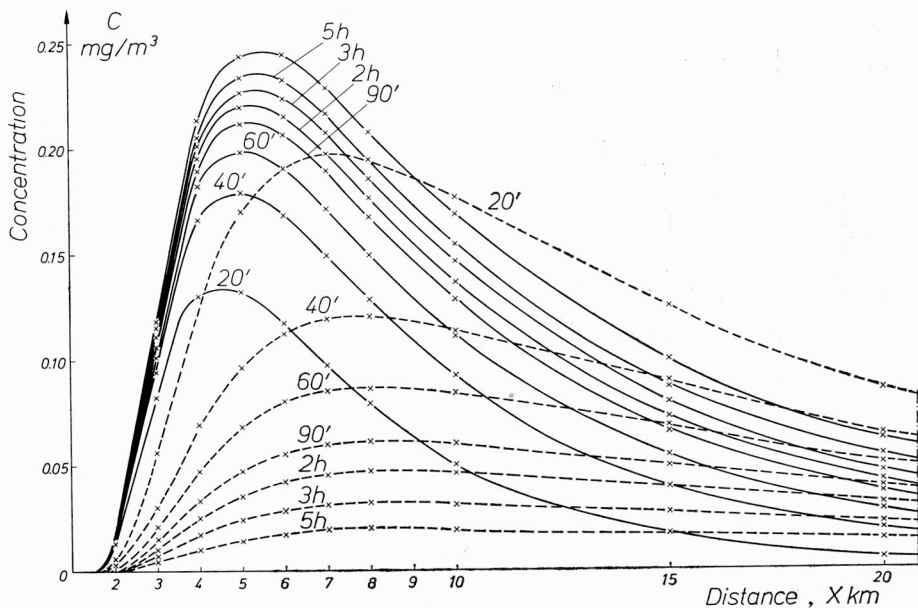


Fig. 3. Atmospheric diffusion of SO_2 and H_2SO_4 ($\tau_{1/2}$, equilibrium state D , $\bar{u} = 3.2 \text{ m/s}$)

— CSO_2 , - - - CH_2SO_4

Rys. 3. Rozkład stężeń SO_2 i H_2SO_4 przy założeniu konwersji dla różnych wartości $\tau_{1/2}$, stan równowagi D , $\bar{u} = 3,2 \text{ m/s}$

— CSO_2 , - - - CH_2SO_4

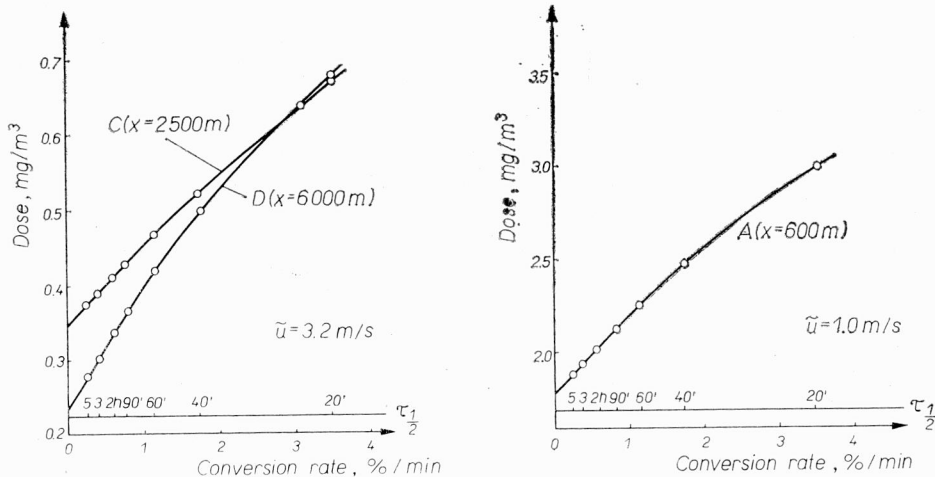


Fig. 4. Maximum SO_2 and H_2SO_4 doses
Rys. 4. Wykres maksymalnej dozy SO_2 i H_2SO_4

and 5 h the increase in the pollution rate related to the maximum values of initial SO_2 concentrations equals 1.73–1.05 (equilibrium state *A*), 1.923–1.070 (equilibrium state *C*) and 2.822–1.166 (equilibrium state *D*).

The H_2SO_4 pollution radius is also significantly increased. At a long distance from the emission source, when H_2SO_4 concentrations exceed the original SO_2 values, the conversion process again contributes to an increase in the pollution rate, which may become 4.5 times that attributed to SO_2 concentrations alone, in the absence of SO_2 conversion.

3. CONCLUSION

The method presented makes it possible to calculate pollution dose variations due to the conversion of SO_2 to H_2SO_4 . Thus, it may be used to determine most disadvantageous conditions when the pollution rate reaches its maximum caused by a simultaneous presence of SO_2 and H_2SO_4 .

If the real conversion time is known, the harmful effect of these compounds on the environment can be easily predicted.

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OBLICZANIE ZMIAN DOZY ZANIECZYSZCZEŃ SPOWODOWANYCH KONWERSJĄ SO_2 DO H_2SO_4

Przedstawiono metodę określania zmian w strukturze pola emisji wywołanych przemianą dwutlenku siarki w trójtlenek siarki, a następnie aerozol kwasu siarkowego. Do obliczeń rozkładu przestrzennego dwutlenku siarki i kwasu siarkowego zastosowano wzór Pasquilla, a zmiany w charakterze emisji oznaczono obliczając dozę zanieczyszczeń przy założonym dowolnym stopniu konwersji. Obliczenia przeprowadzono dla huty miedzi, gdzie ze względu na emisję pyłów metalicznych katalizujących konwersję dwutlenku siarki problem ten ma szczególne znaczenie.

Stwierdzono znaczny wpływ stopnia konwersji tak na zwiększenie dozy zanieczyszczeń, jak i zasięgu szkodliwego oddziaływania źródła. Opisana metoda może służyć do znalezienia najbardziej niekorzystnych warunków, w których występuje maksymalna doza zanieczyszczeń pochodząca z równoczesnego występowania dwutlenku siarki i kwasu siarkowego.

BERECHNUNG DER VERÄNDERUNG DER SCHMUTZLAST BEI KONVERSION VON SO_2 ZU H_2SO_4

Dargestellt wird eine Methode zur Bestimmung der Wechselvorgänge in der Struktur des Immissionsfeldes, die durch die Konversion von SO_2 zu SO_3 und nachfolgend zum Aerosol von H_2SO_4 verursacht werden. Die Ausbreitung von SO_2 und H_2SO_4 wird mittels der Pasquille-Formel berechnet; die Änderungen im Immissionscharakter bestimmte man durch Berechnung der Schmutzlast bei beliebig angesetztem Konversionsgrad. Als Rechnungsbeispiel diente eine Kupferhütte, da bei der Emission von Metallstäuben die katalytisch wirken, der Konversion von SO_2 besondere Bedeutung zukommt.

Festgestellt wurde der bedeutende Einfluß des Konversionsgrades und das sowohl in Hinsicht auf die zunehmende Schmutzlast, wie auch auf die Reichweite der schädlichen Einwirkung der Emissionsquelle.

Die beschriebene Methode kann zur Festlegung ungünstigster Verhältnisse dienen. Die maximale Schmutzlast kommt dann vor, wenn SO_2 und H_2SO_4 gleichzeitig anwesend sind.

РАСЧЕТ ИЗМЕНЕНИЙ ДОЗЫ ЗАГРЯЗНЕНИЙ, ВЫЗВАННЫХ КОНВЕРСИЕЙ SO_2 В H_2SO_4

Представлен метод определения изменений в структуре области проникновения имиссии, вызванных превращением двуокиси серы до серного ангидрида, а затем аэрозоля серной кислоты. Для расчета пространственного распределения двуокиси серы и серной кислоты применена формула Паскилла, а изменения в характере проникновения определены путем расчета дозы загрязнений при предположенной произвольной степени конверсии. Расчет произведен для медеплавильного завода, где из-за эмиссии металлических пылей, катализирующих конверсию двуокиси серы, эта проблема имеет особое значение.

Обнаружено значительное влияние степени конверсии как на увеличение дозы загрязнений, так и радиус вредного воздействия источника. Описанный метод может использоваться для определения наиболее неблагоприятных условий, при которых образуется максимальная доза загрязнений, происходящая от параллельного появления окиси серы и серной кислоты.