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A NEW SULPHUR DIOXIDE CONVERTER

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A few years ago the modernising of one of our sulphuric acid plants was started with the erection of two pyrites turbulent bed furnaces.

The roast gases from the furnaces contain 10 - 12 % sulphur dioxide in contrast to the 7% which was the highest concentration that could be obtained with the old hearth roasters. This resulted in an increased capacity in the gas cleaning system of the sulphuric acid plant. In order to make full use of this additional capacity it was necessary to build a new converter. At the same time it was decided that some of the old converters should be discarded, and the new converter had to be designed for a capacity of at least 100 tons of sulphuric acid per 24 hours.

The floor space available in the sulphuric acid plant for this new converter was only 7 by 8 metres. Within these limits the converter and the necessary equipment for operation and maintenance had to be built.

To our knowledge there was no commercially available sulphur dioxide converter of the desired capacity that could be built on the available floor space. One of the authors therefore initiated the development of a converter that could be designed utilizing experiences from modern waste-heat boilers. The following arrangements had to be made.

1.   The converter had to be built as a tower with a rectangular cross section.

2.   The catalyst had to be divided into several layers and if possible the catalyst to be provided for a 20% overload (100 ton H_2SO_4 + 20 ton H_2SO_4).

3.   Heat exchangers had to be built in between the catalyst layers in order to control the temperature at the optimum at all points in the converter. The heat exchangers had to be built as standardized units.

4.   The primary heat exchanger for the cold entering gas and the hot converted gas had to be entered in the lower part of the tower.

Furthermore:

5.   The heat of the reaction should be utilized for steam

generation.

6.   The total pressure drop across the converter and the heat exchangers should be around 500 mm water column, not exceeding 700 mm water column.

7.   The starting device should also be capable of holding the converter at reaction temperature for several days, should any breakdown of the roast furnaces occur. (The number of roast furnaces had been decreased from 8 to 2 and the possibility of an interruption of the service was considerable.)

Kinetic Design.

One of the authors has performed a detailed study of the rate of oxidation of sulphur dioxide over a technical vanadium-potassium catalyst so that the calculation of the amount of catalyst and optimum temperature profile in sulphur dioxide converters could be performed. At that time no reliable information had been published about the rate of oxidation of sulphur dioxide over vanadium catalyst of technical size and composition.

Rate measurements, aimed at a relation that describes the rate as a function of composition, pressure and temperature, are best performed in a differential reactor. The necessary apparatus for the study of this particular flow reaction was built on a very small laboratory scale and employed a catalyst bed containing only 1.7 g of catalyst. The rate expression developed from the experimental data was then applied to rate measurements obtained with catalyst beds composed of catalyst particles of technical size and the rate constant was calculated. For further details of the investigation we refer to the literature (1).

Fig. 1

Fig. 1 shows the measured relation between the rate of the reaction and the partial pressure of oxygen. It is apparent that the rate is directly proportional to the partial pressure of oxygen. It is, however, to be observed that this holds as long as the partial pressure of oxygen is kept below about 0.15 atm. At temperatures below about 450°C and at partial pressures of oxygen above 0.15 atm. the rate has been found in experiments to be proportional to the second power of the partial pressure of oxygen. Therefore at low temperatures the following rate expression is only valid when the partial pressure of oxygen is below about 0.15 atm.

Fig. 2

Fig. 2 shows the rate of the reaction plotted as a function of the square root of the partial pressure of sulphur dioxide. It is observed that the rate may be described as directly proportional to the square root of the partial pressure of sulphur dioxide.

Fig. 3

Fig. 3 shows the rate of the reaction plotted as a function of the inverse of the square root of the partial pressure of sulphur trioxide. It is observed that the rate of the reaction is proportional to $1/\sqrt{PSO_3}$, which means that the rate of the reaction decreases with increased partial pressure of sulphur trioxide much more noticeably than as a result of the reverse reaction alone.

If these observations are combined with the observation from rate equations derived theoretically - that the expression for the driving force inside the brackets must be in the form indicated if the determining step for the slow rate is the reaction between

oxygen and the active component of the catalyst - then a possible rate equation will be

$$r = k \cdot \sqrt{\frac{P_{SO_2}}{P_{SO_3}}} \left(P_{O_2} - \frac{P_{SO_3}}{P_{SO_2} K}^2 \right) \qquad \frac{gmole \ SO_2}{(g \ catalyst) \ (sec)}$$

This rate equation has been experimentally found to describe the rate of oxidation of sulphur dioxide over vanadium-potassium catalysts within the temperature interval of 440 to 550°C, partial pressures of oxygen up to 0.15 atm., of sulphur dioxide up to 0.08 atm. and of sulphur trioxide to 0.06 atm. It has also successfully been applied to vanadium-potassium catalysts of different composition with regard to weight percent V_2O_5 and mole ratio K/V. It was found that a minor change in the composition of the catalyst with regard to the active components had no significant influence upon the activity of the catalyst.
Fig. 4.

Fig. 4 presents the rate constant as a function of the temperature for three different particle sizes. The first two curves are for small-sized catalyst particles investigated on a laboratory scale. Curve number three was calculated from a large scale experiment. Based on the given rate equation and the experimentally determined rate constant it is possible to calculate the rate as a function of composition and temperature. Fig. 5 shows such a rate diagram for a gas containing 7% sulphur dioxide, obtained from pyrites. In this diagram no correction has been made for the diffusional resistance. The influence of the diffusional resistance in the gas phase is normally rather small.

For a design calculation we need to know the temperature in a converter as a function of the conversion. If we as an example assume adiabatic reaction and no heat transfer in the direction of gas flow, then a diagram may be constructed giving the temperature of the gas phase as a function of conversion. Fig.6 shows the reaction temperature as a function of conversion for a gas of the indicated sulphur dioxide content. The equlibrium lines have been included in the diagram and also the lines of optimum reaction temperature. In this diagram the reaction is assumed to start at 450°C and zero conversion. It will be found that if the reaction is assumed to start at any other temperature and conversion, the adiabatic operating lines will be almost parallel to the line given in the diagram.

Applying a material balance around a differential layer of catalyst, we are now in the position to calculate the amount of catalyst necessary for any feed rate and desired conversion, and to arrive at the optimum temperature for any operation.

Mechanical Design.

Fig.7

The general design is shown in Fig.7. The external dimensions of the converter are: height to the top of the gas entrance duct 19.5 meter, and external cross section 4.7 x 4.8 m².

The converter is erected on five vertical supporting columns, one of which is placed in the centre of the structure and the other four in the corners. The colums have a square cross section and are hollow. Hot gases circulate round the entire centre column. In order to avoid thermal stress in the corner columns they have been constructed open inside so that they will attain the same temperatures as the hot gases. At the top of the catalyst layers, however, the hollow spaces in the columns are shut, to force all the gas through the catalyst layers. In the lower part of the converter where the temperature is low, the columns are stiffened and closed, bearing in mind the possibility of corrosion. Only the central column is rigidly fixed to the ground, the corner columns rest on rollers moveable in the direction of the diagonals.

The inner walls of the casing are composed of buckled sheet iron profiles, welded together along the outer edges of their flanges. Th makes the inner casing so resilient that it can withstand possible the stress. The inner casing is covered with a thick layer of fiberglass insulation and outer cover plates on a framework. This framework is moveable in relation to the inner casing.

Around the catalyst layers the inner walls are protected with a thin bricklayer, and the bottom of the converter is covered with an ac proof brick lining.

The catalyst layers rest on perforated sheets, covered with a wi screen and a thin layer of silica pebbles, all supported by beams. T supporting beams have been given crossections that will promote the turbulance of the gases.

The gas to gas heat exchangers are composed of a number of standardized tubular units. This simplified manufacture, assembly an a possible exchange of any of the units in the future. The heat exchangers for the excess heat of the reaction are likewise constructe as standardized units of high pressure boiler tubes. Saturated high pressure steam from the waste heat boilers after the pyrites furnaces i employed as a cooler. The generated superheated steam is cooled to t desired temperature by injection of condensed water. The recovered h from the process may thereby be obtained as saturated or superheated steam.

Starting Device.

One of the basic requirements was that the starting device coul be used to hold the converter at reaction temperature, should both the pyrites roasters break down and be shut off more than two days. Neve: theless it was expected that the starting device should not be used m than a couple of weeks during a period of 10 years, (as is the practi for large sulphur dioxide converters). Then it is evident that it i more important to arrive at a low investment cost for the starting de than to obtain low operating cost.

From the investment point of view the cheapest arrangement was supply the heat as electric power. When the starting device has to used the total installed power in the plant is not employed. As a result electric power is available, and this power may be used for he generation.

Dry air is electrically heated in a chamber containing a large number of resistant heated Ni-Crome elements, protected against gas i thin alloy steel tubes. The hot air then passes all the catalyst layers. The heat exchanger in the lower part of the converter is use during the starting period to preheat the cold dry air with the hot a that has passed the catalyst layers, as is shown in Fig.8.

When starting a new converter the fresh catalyst is pre-dried with dry air. When the outgoing air reaches the same low moisture content as the incoming dry air, steam is admitted to the steam coils in the converter, and the stream of dry air is indirectly preheated w the steam. When temperature equilibrium between the steam and the h dry air stream is approached, power is admitted to the electric air heater and the steam is shut off, in order to avoid any cooling by th steam. When reaction temperature has been reached, the starting dev is sealed off, and the cooling steam and the roast gases are admitted The ignition temperature for this converter is between 370° and 380° C

Performance

Based on the kinetic study it was calculated that the converter should be provided with five layers of catalyst and the total catalys requirement was about 20 tons. This should allow a possible overloa of 200% and a conversion of 98%. The catalyst employed in this conve

is composed of cylindrical particles with diameters of 7 - 8 mm and heights of 10-30 mm.   It was also checked that the built-in heat exchangers should allow safe and stable operation at different sulphur dioxide concentrations in the roast gases.

The conversion obtained is 98% at the rated capacity, and the calculated temperature profile seems to coincide with the actual performance of the converter.   Production capacity may be changed from about 40 tons/day to well above 120 tons/day.   The total pressure drop across the converter is 570 mm of water at normal capacity.

Generated steam amounts to 1.1 ton/hr saturated steam of 23.5 ata (feed water 90°C) at normal capacity.   Heat losses through the walls of the converter are very small, about 30 kcal/m²hr.   Feed gas temperature is 55°C and the gas leaves the converter at 140°C.
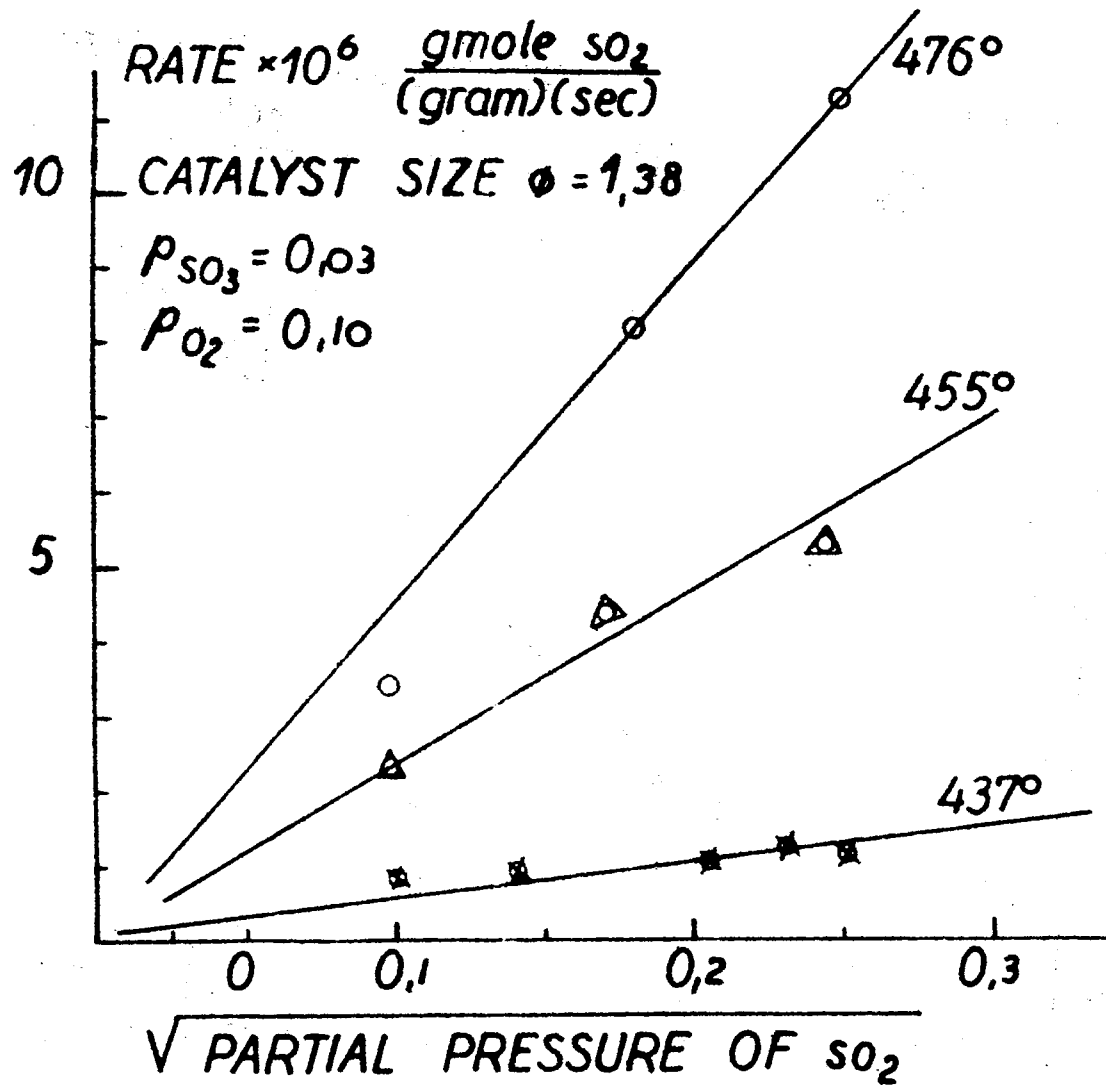
The converter has been built by AB Svenska Maskinverken, Södertälje, Sweden, according to our design.   A number of details of the converter are subject to patent applications in different countries.
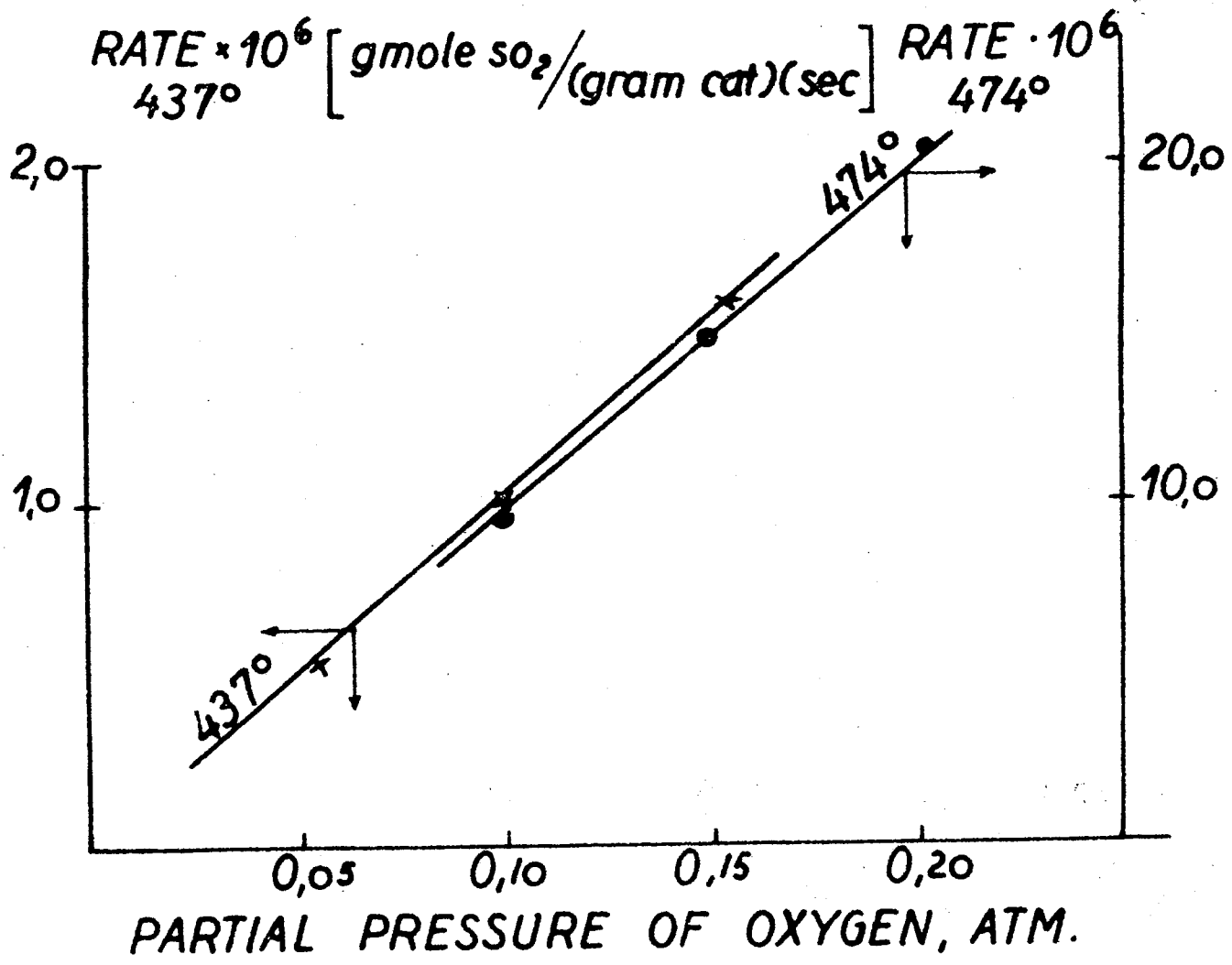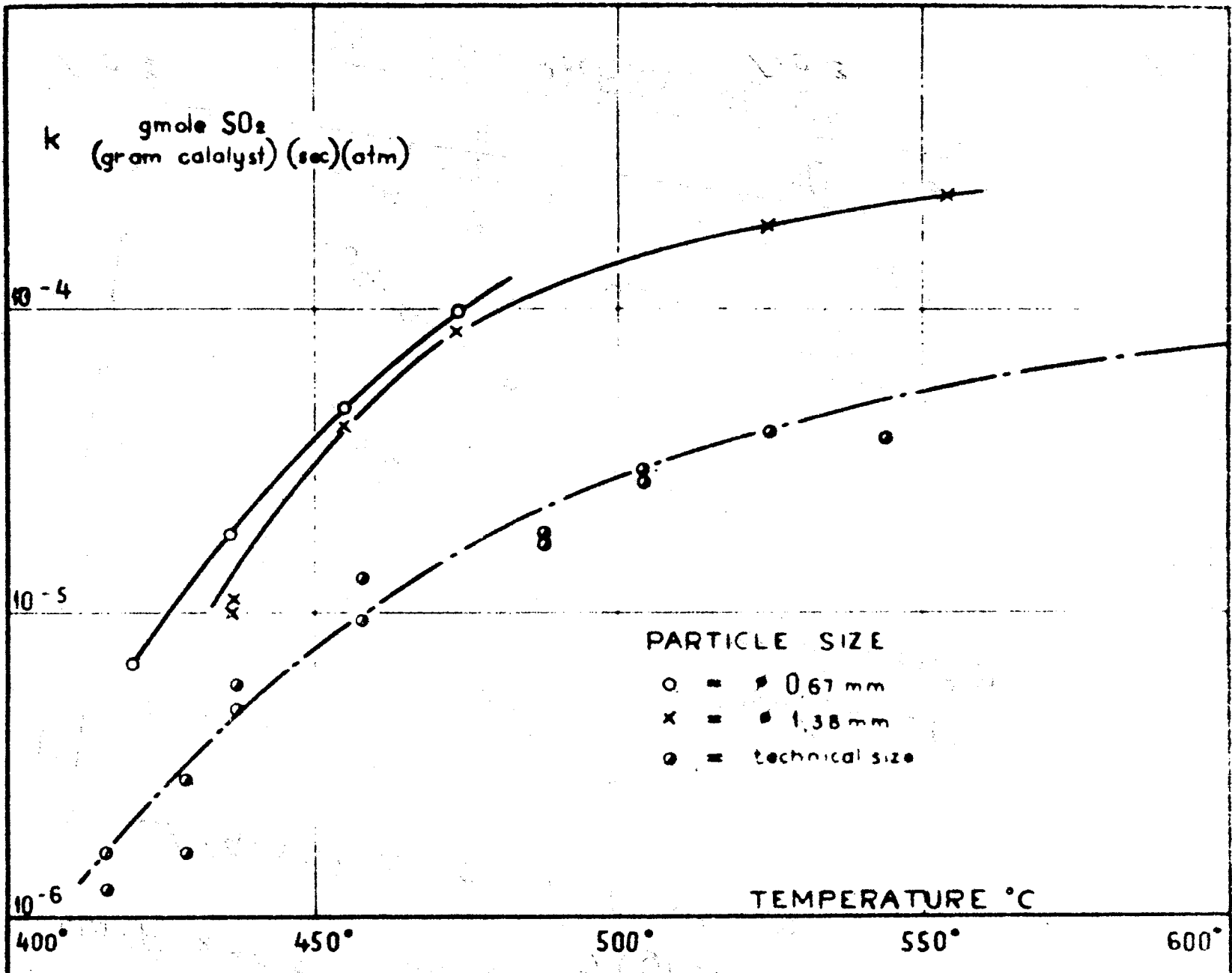
Literature:

Eklund, R.-B.   The rate of oxidation of sulfur dioxide with a commercial vanadium catalyst.   Almqvist & Wiksells, Boktryckeri AB, Stockholm, 1956.

SUMMARY

A brief description of the construction of a new sulphur dioxide converter is given in which experiences of modern exhaust steam boilers have been exploited. A special characteristic is that the converter requires very little space, while the height is somewhat greater than usual. For the dimension of the catalyst layers a detailed kinetic study of the vanadium-potassium catalyst was performed, the result of which is briefly mentioned.

RATE ×10⁶ $\dfrac{gmole\ SO_2}{(gram)(sec)}$

CATALYST SIZE ⌀ = 1,38

$P_{SO_3} = 0,03$

$P_{O_2} = 0,10$

476°

455°

437°

10

5

0   0,1   0,2   0,3

√ PARTIAL PRESSURE OF SO_2

RATE × 10⁶ [gmole SO₂/(gram cat)(sec)]

PARTIAL PRESSURE OF OXYGEN, ATM.

Rate constant as a function of temperature °C

RATE × 10⁶   gmole SO_2/(gram)(sek)

CATALYST SIZE, $\phi = 0,67\,mm$

474°

$p_{O_2} = 0,10$ atm
$p_{SO_2} = 0,014$ atm

455°

437°

420°

10

5

0   5   10 ⟶

$1/\sqrt{}$ PARTIAL PRESSURE OF SO_3