Introduction

Sulphuric acid still remains a bulk product. World production of sulphuric acid reaches some 200 million tonnes, the figure for Poland is ca. 2 million tonnes [1]. The principal use of sulphuric acid is still the manufacture of phosphate fertilizers, where its role is to convert phosphate rock into calcium dihydroorthophosphate, which is water soluble and assimilable by plants.

The progress made in sulphuric acid manufacture during recent decades has led to changes in the method and technology of its manufacture [2], resulting mainly in the reduction of emissions of sulphur compounds to air and reduction of harmful waste [3].

Having regard to social requirements, the environmental impact of this production has been abated. It may therefore be assumed that the present knowledge of sulphuric acid manufacturing process is deep.

Is it then right to say that there is nothing left to be done in the domain of sulphuric acid? This certainly is not true.

Manufacture of sulphuric acid comprises a number of interdependent operations and processes. All of these must be performed with maximum efficiency, which requires the application of the most up-to-date solutions enabling compliance with legislation, while bearing in mind that the slowest process controls the overall rate.

Development strategy

The European Sulphuric Acid Association recommends further development of techniques aimed at improving manufacturing processes and modernising sulphuric acid plants in order to reduce their environmental impact [4].

The assessment of the progress and of the needs and requirements enables to indicate the main paths of development this industry should follow:

1. Process optimisation.
2. Manufacturing technology.
4. Design of contact and absorption sections.
5. Diversification of SO₂ utilisation methods.

Another issue is waste management. A separate paper will be devoted to this problem.

Process optimisation

There is an on-going tendency to extend the production cycles of sulphuric acid plants. This is associated with the difficulty to maintain optimum parameters when the duration of the manufacturing process is extended, leading to process disturbances and increased emissions of sulphur compounds. The consequence of these changes is also the loss of the autothermal nature of the process and increasing emissions along with decreasing profitability of manufacture.

Maintenance of operating parameters in an extended production cycle, which ensures low sulphur emissions, is particularly difficult in metallurgical plants. It is therefore necessary to optimise parameters of all processes occurring in the manufacture of sulphuric acid.

The first of such processes requiring optimisation is the treatment of process gases - this applies to metallurgical type plants. This gas contains solid and gaseous impurities that are harmful to further stages of acid manufacture, and must therefore be removed from the gas. As a result of the applied method of gas treatment, waste acid scrubber liquid is generated. This acid contains metal contaminants derived from the processed ore concentrate, except for the metal that is recovered. As the waste acid is deposited in a semisolid waste disposal site, which is a very costly operation, optimisation of the gas treatment process should warrant maximum possible gas purity, with minimum volume of waste generated. In case of some types of apparatus used, it is not possible to increase the concentration of the washing acid solution, therefore optimisation plays a particularly important role. As the performance of the process system is a compromise between the efficiency of washing and the concentration of the washing solution, it is therefore necessary to take into account the specific characteristics of the manufacturing process [5-7].

Another process that requires optimisation is the absorption of moisture and sulphur trioxide. Optimisation is required because of the dependence of the absorption process efficiency on mass and volumetric load on the scrubbers that increases with the manufacturing cycle duration [8]. Such dependence is always followed by decrease in process efficiency. Increased moisture content in the processing system may lead to excessive corrosion and deactivation of the vanadium catalyst, whereas increased SO₃ content in the gas causes higher SO₂ emissions, decreased efficiency of SO₂ oxidation (increased SO₂ emissions) and higher risk of processing system corrosion. The apparatus will operate properly only when these interdependencies are defined, and steps will be undertaken to mitigate the impact thereof on the processes effected.

The most important process in sulphuric acid manufacture is the oxidation of SO₂ to SO₃. The efficiency of this process decreases relatively fast, producing undue process and environmental effects. The recommended best available technique is the use of a caesium catalyst in the first and last beds of the catalytic reactor. The disadvantage of this solution is the extremely high cost of the catalyst and lack of warranty of maintaining high catalytic properties with increasing amount of iron introduced into the active phase, which occurs particularly in metallurgical type sulphuric acid plants.

The strategy of sustainable development of sulphuric acid manufacture should be bound to optimisation of the distribution of the catalyst in the beds in the catalytic reactor, with account taken of the actual catalytic properties, capability of effective heat exchange in exchangers and establishment of operating temperature ranges for the individual beds ensuring that the process is autothermal [8]. Application of this technique will allow to safely extend the production cycle without standstills and without increasing sulphur emissions to air.

Technology

According to BAT, shifting to multistage processes is the proper way of reducing sulphur dioxide emissions to air. Thus, the technology of the future is the multistage triple contact-triple absorption (TC/TA) technology (Figs. 1, 2) [9].

It enables increasing the efficiency of the SO₂ oxidation process to 99.99% at 12-18% SO₂ concentration in gas, while sulphur emission to air is many times lower than that in double contact-double absorption (DC/DA) process, and only to a small extent depends on the duration of the production cycle. This warrants improved sulphur consumption and catalyst amount rates 160-180 dm³/t MH²/24h. This technology is particularly promising for metallurgical plants, as it enables reducing...
the size of apparatus and gas piping, improving sulphur recovery and power consumption rates, minimising stack construction cost, while improving metal and acid production output and complying with emission limits. The attractiveness of this solution lies in the economic and environmental benefits it offers.

There are now foundations for implementing this technology in the plants, and the strategic actions should be devoted to developing the most efficient contact and absorption sections.

Catalysts

The composition of the active phase of vanadium catalysts determines their catalytic activity and ignition temperature [10]. Thus the composition and properties of the active phase determine the suitability of the catalyst for the industrial process.

For the various operating conditions, catalysts can be promoted with various alkaline compounds, e.g. Na or Cs, which change the properties of the active phase and thereby change the catalytic properties thereof under defined conditions. If we assume that the generic chemical formula of the active phase is K\textsubscript{1}Me\textsubscript{1-x}V(SO\textsubscript{4})\textsubscript{2} and K\textsubscript{1}Me\textsubscript{1-x}V(SO\textsubscript{4})\textsubscript{3}, then Me denotes Na, Cs, as well as undesired contaminants, e.g. Fe. The composition of the active phase changes with temperature and reaction environment. Introduction of, for instance, caesium compounds, causes melting of the Cs-containing part of the phase at a lower temperature and initiating the SO\textsubscript{2} oxidation process – lower catalyst ignition temperature. If the resulting rise of temperature is sufficient to cover the loss of heat, then the catalyst layer starts working at a slightly lower temperature. On the other hand, oxide or sulphate iron (of corrosion) increases the melting point of the active phase, depending on iron content. On the one hand we lower the ignition temperature of the catalyst by intentionally modifying the active phase, and on the other hand, the ignition temperature is increased due to unavoidable introduction of iron into the active phase. This means that it is not possible to describe deactivation and deterioration of performance of the catalysts by means of mathematical algorithms and that it requires a different approach.

Research on catalysts should be focused on low-temperature systems, less susceptible to structure and texture change caused by operating conditions. The caesium-modified catalyst of lower ignition temperature and higher reaction rate at low temperatures (360-400°C) recommended by BAT does not meet such requirements [10].

Solutions that radically change catalytic properties of a catalyst or the oxidation mechanism by, among other factors, taking advantage of the properties of some chemical substances, may form grounds for revolutionary changes in industrial catalysis.

Design of contact and absorption sections

The design of the contact and absorption section is pivotal to achieving the autothermal course of the process. In sulphur processing plants autothermality in the staged DC/DA process may be achieved at SO\textsubscript{2} concentration of 6%. The implementation of this autothermal technology in metallurgical type sulphuric acid plants was extremely difficult due to high variability of the composition, flow rate...
and temperature of the process gas. This process was resolved by buffering the inter-stage distribution of heat downstream of the 3rd catalyst bed in the converter and imposed by the design of existing 3 + 1 bed arrangements in converters, although this is not an optimum solution.

Strategic solutions for metallurgical type sulphuric acid plants should be based on a different inter-stage distribution of process heat. Three practical embodiments of this concept exist. One consists in controlled increase of the quantity of catalyst in the 2nd bed and providing the ability to take over the load from the 1st bed as the production cycle duration is extended. The second solution consists in controlled transfer of the load onto the 2nd bed of the converter – this requires change in gas circulation in the converter. The advantage of this solution is the number of heat exchangers downstream of the 1st bed. The disadvantage is flexibility in heat transfer.

The most rational solution seems to be the exploitation of the so-called kinetically dynamic state existing between the 1st and 2nd catalyst beds in the converter and using part of the heat from the 1st bed to heat the process gas and the gas from the inter-stage absorption (Fig. 3). The attractiveness of this concept lies in efficient inter-stage distribution of SO$_2$ oxidation heat. Initially the first bed operates at higher conversion rate and the quantity of heat used for heating the gas fed to the 2nd contact stage is higher. When conversion in the 1st bed drops, the quantity of heat from the 1st bed is lower; but the conversion rate in the 2nd bed increases, and consequently the quantity of heat used for heating the gas fed to the 2nd contact stage also increases. This enables, in the initial period of the cycle, to heat the process gas going to the 1st bed, with maximum transfer of heat from the dynamic bed system to heat gas going to 4th bed. Decreased conversion on the 1st bed increases conversion on the 2nd bed, which changes the temperature range of bed operation. This reduces quantity of heat transferred from the 1st bed, while the quantity of heat transferred in heat exchanger E205 after the 2nd bed for heating the gas from inter-stage absorption is increased. The dynamic system enables, in the final period of the production cycle, to transfer optimum quantity of heat after the 1st bed, with maximum quantity of heat transferred after the 2nd bed.

Diversification of SO$_2$ utilisation methods

After the transformation of the economic system in Poland, the sulphuric acid industry goes through intermittent difficulties in bringing the supply into balance with the demand. In case of oversupply, the metallurgical plants face the risk of metal production stoppage. The strategy of sulphuric acid manufacture development calls for ways of balancing sulphuric acid supply and demand. It is then reasonable to prepare a proper buffering solution consisting in reducing acid production in favour of processing sulphur compounds into other marketable products, while maintaining the control over acid demand and supply in the country.

There are a number of methods and proven processes for removing sulphur dioxide from gases, applied mainly in the power industry, consisting in SO$_2$ absorption and generation of various commercial products. Some of these methods have been tested in sulphuric acid plants to remove sulphur dioxide from waste gas from the manufacture of sulphuric acid under high load of gaseous SO$_2$ or under the conditions of single contact/single absorption technology. There are also other proven solutions of using SO$_2$ from sulphuric acid plants for other purposes, e.g. for the manufacture of liquid sulphur dioxide.

However, there are no solutions and methods of processing sulphur trioxide from the waste gas from sulphuric acid plants, apart from oleum manufacture.

When developing a solution, the existing conditions have to be taken into account, such as: SO$_2$ emission limits, maintaining the process completely autothermal, design parameters (active surface of the converter, linear velocity of gas, distribution of catalyst, production volume, kinetic and thermal conditions of the process), expectations of plant operators with regard to reducing volume of acid production and marketability of products.

A preferable solution to the diversification of sulphur dioxide use is the manufacture of sodium bisulphate, liquid SO$_3$, or oleum. However, when implementing these solutions, one must take into account the saleability of these products.

Another advantageous solution may also be the manufacture of synthetic gypsum, both using sulphur dioxide (process gas entering the sulphuric acid plant) as well as mixture of sulphur trioxide and sulphur dioxide (process gas after 1st catalyst bed). When considering this concept, account has to be taken of conditions, such as SO$_3$ absorption efficiency, chemical homogeneity of the product, content of metallic contaminants specific for the production process and contaminants specific for the catalyst, moisture and water content in commercial product. Other problems also have to be resolved, such as: heat of SO$_2$ sorption in solutions and volume of wastewater and treatment thereof, removal of sulphuric acid drops and mist from post-reaction gas, removal of excess moisture from post-reaction gas, mass transfer conditions warranting higher efficiency of SO$_2$.
absorption at higher concentrations of the removed component in gas, provision of conditions for complete oxidation of sulphites in case of $\text{SO}_2$ sorption at higher content thereof in gas.

Summary

The strategy of production safety for sulphuric acid plants should be associated with:

- Research on process optimisation aimed at stabilisation of sulphur emissions to air during the extended production cycle in line with BAT guidelines
- Undertaking research on reducing sulphur emissions to air by changing the technology – recommended by BAT
- Seeking new possibilities in the field of catalysts, associated with change in catalyst structure and texture, modification of geometric structure of active sites or surface clusters to improve oxygen transport between reagents and lower ignition temperature of the catalyst
- Novel solutions of converter and absorption sections, enabling to take advantage of the kinetically dynamic state of the 1st and 2nd bed in the converter to optimise the inter-stage distribution of heat
- Seeking solutions aimed at diversifying $\text{SO}_2$ removal methods, to free metal production from variations in acid demand and supply.

Literature


Piotr GRZESIAK - Prof.(Ph.D.), graduated from the Faculty of Chemistry of the Adam Mickiewicz University in Poznań. Head of the Institute of Environmental Protection - National Research Institute in Poznań. Specialist in process technology, environmental engineering and environmental protection. For many years he has been leading a research team carrying out studies on environmental technology and engineering and implementing research results in the industry. Certified expert on chemistry. Obtained 2nd degree professional specialisation in industrial catalysis. Awarded a Gold Medal with distinction at the International Exhibition of Inventions, Research and Industrial Innovations Brussels-Eureka and a Certificate of Appreciation from the Chairman of the State Research Committee for the contributions to the development of the Polish Science.