Trends of sulfuric acid production in metallurgical installations

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Please cited as: CHEMIK 2010, **64,** 6, 462-469

Introduction

At present, Poland is one of the biggest producers of sulfuric acid. In 2007 production of sulfuric acid in Poland was 2 mln T monohydrate (MH)/y, what means 2nd place in Europe and 7th place in the world [1]. Almost half of its production comes from metallurgical installations.

In last decades a huge advance in production of sulfuric acid was made in the result of implementation of new technological solutions that consisted in changing of methods and technologies of sulfuric acid production as well as in reduction of emission of sulfur compounds and reduction of volume of deposited harmful wastes [2].

Nowadays by advance of technology we mean not only technical and technological improvement or optimization of the process, but also the measures that are important in elimination of impact of production process on the environment [3, 4].

Technology of sulfuric acid production is very well known and its further improvement is more and more problematic due to the necessity of following rules of economy and requirements regarding impact on the environment. Joining of Poland to European Union resulted in a necessity to specify the impact of technology on natural environment as well as in showing the measures that can reduce or completely eliminate its negative effects [5, 6].

During roasting of zinc, lead or copper ores, huge amount of gases that contain, apart of sulfur dioxide, significant amounts of dust and small amounts of sulfur trioxide as well as other harmful gaseous contaminants that depend on composition of processed concentrate, are generated. Presence of those harmful gases in process gases directed to the sulfuric acid plant is not acceptable.

Purification of process gases

The installation of purification of process gases produced in the process of roasting of non-ferrous metals ores is most important part of preparation of the gas to be converted into sulfuric acid in installations of metallurgical type. Condition that can be found in the roaster cause penetration of dust, aggressive sulfur compounds (SO_x) and other harmful gaseous substances (HF, HCl) to the gas.

The process gas after leaving the roaster is cooled in a boiler and then purified in dry electro-filters. Initially purified gas undergoes further purification by a wet method in washing installation and in wet electro-filters and then it is dried in a drying installation. The gas without all contaminants is then directed to sulfuric acid installation.

Variety of contaminants as well as necessity of precise purification of the gas requires implementation of more and more efficient washing installations like Swemco shelf scrubber with double circuit (Fig. 1), MONSANTO DynaWave scrubber (Fig. 2) or scrubbers of Lurgi Venturi, or RFS radial scrubber (Fig. 3) [7÷9]. Two-stage washing and cooling of the gas is a common solution used nowadays. First stage is a scrubber, in which dust is removed by injection of liquid into a gas stream and it is adiabatically cooled, and the second stage is a cooling tower with packing. All the solutions of installations were used in Polish sulfuric acid plants. Swemco scrubber is successfully used in ZGH BOLESŁAW in Bukowno, DynaWave scrubber operates quite recently in Huta Miedzi [copper smelter] LEGNICA, and RFS scrubbers work successfully in Huta Miedzi GŁOGÓW, both in the case of stable gases (Huta Miedzi GŁOGÓW II), and not stable gases (Huta Miedzi GŁOGÓW I).

Each design of gas washing installation has its advantages and disadvantages, so their proper selection that takes into account production specificity of plants is very important. There are no universal solutions.

Using more efficient washing facilities and their proper selection has an impact on length of production cycle. A selection that takes into account gas properties (temperature, content and character of removed contaminants, changeable flow rate) as well as operational conditions of installation (erosion and corrosion of most of constructional materials) is especially difficult. Dust should be removed from the gas to the level of about 30-50 mg/Nm^3 and gas should be cooled to the temperature 30-35°C. Fluor content in the gas should not exceed 2 ppm due to a possibility of serious contamination of acid coolers, linings, demisters, ceramic packaging and catalyst. Fluor and chlorine in the process gas are especially harmful during production of sulfuric acid.

It seems to be economically justified to use DynaWave scrubbers or Venturi scrubbers as well as verified solutions of SWEMCO scrubbers in the case of stable gas flow or if its flow rate changes slightly.

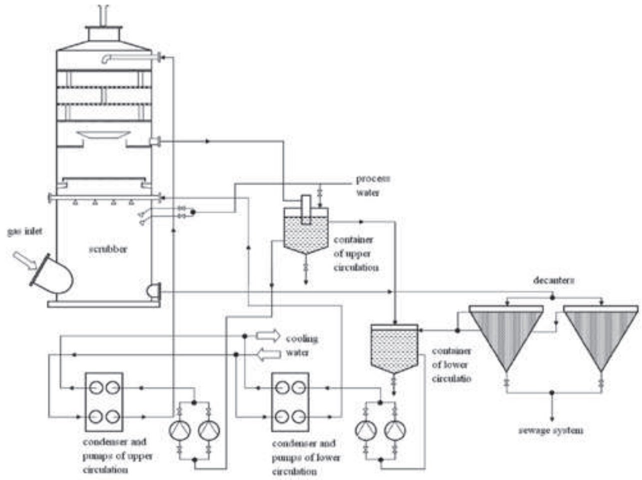

Fig. 1. Diagram of cooling and washing installation with SWEMCO scrubber

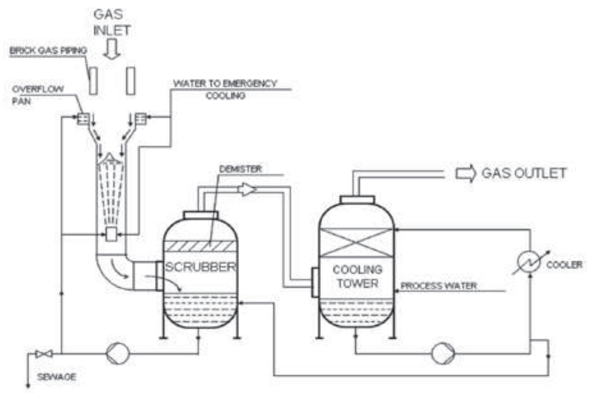

Fig. 2. Diagram of cooling and washing installation with DynaWave scrubber

When gas flow rate changes significantly or if there is a flow pulsation, the best solution is to use RFS scrubbers of radial gas flow to obtain assumed dust control efficiency at optimal gas pressure drop and stabilization of flow after the scrubber, which has a positive impact on operation of wet electro-filters.

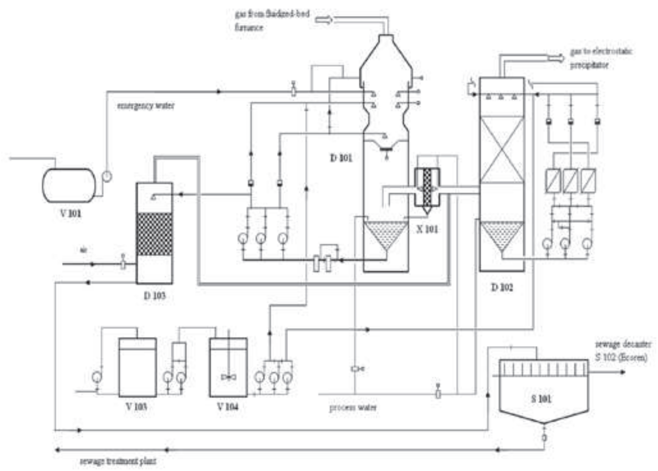

Fig. 3. Diagram of cooling and washing installation with RFS scrubber

Absorption of water and sulfur trioxide

In all Polish installations the absorption process is realized in a concentrated sulfuric acid solution in towers operating in a countercurrent system [7]. The installation guarantees drying out of air below 0.02 g H_2O/Nm^3 and the process gas below 0.2 g H_2O/Nm^3 and absorption efficiency of SO_3 is above 99.9% in each type of installation.

Design of towers can be traditional with supported grate or state-of-the-art one with self-carrying grate (Fig. 4). Those two solutions are used in Polish installations, but traditional solution prevails. Self-carrying grate is used in a drying tower and in absorption towers in Huta Miedzi GŁOGÓW II. Ceramic elements of different shapes are used as packing, but now already piled.

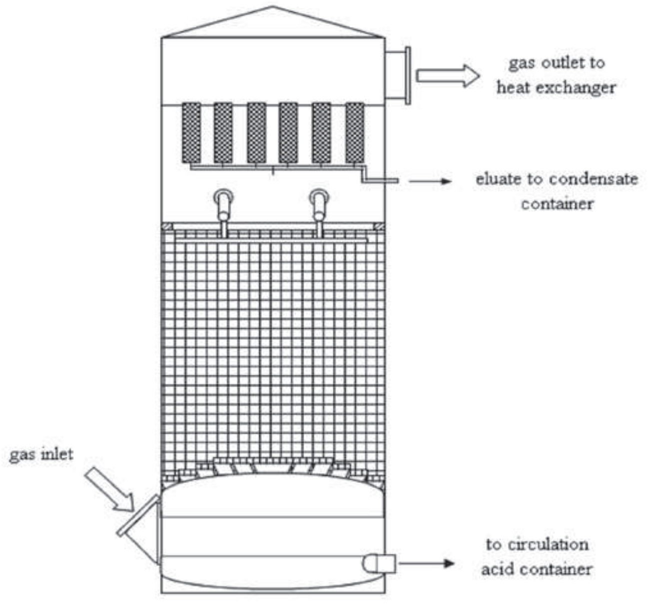

Fig. 4. Absorption tower with self-carrying grate

In all Polish installation the absorption towers are equipped with high efficient demisters that are used to remove sulfuric acid mist and drops from gases. In majority of sulfuric acid factories demisters made by OMEGA Bielsko Biała of very high quality are used, they also deliver demisters resistant to fluor.

In some of the plants operational parameters of drying-absorption installations are optimized. It is worth to remember that use of such technology gives measurable benefits such as increase of life of catalyst used for oxidation of SO_2 (reduction of wastes volume), reduction of SO_3 emission (lower fees and fines for use of the environment) as well as increase of thermodynamic efficiency of converter – reduction of SO_2 emission - lower fees and fines for use of the environment. Optimization of absorption process parameters carried out in some Polish factories enables, among others, extending the production cycle even up to 4 years without any consequences of increase of SO_x emission, which was not possible long time before.

Technologies of sulfuric acid production

BAT Directive contains a review of SO_2 oxidation technologies and main criterion of their use is concentration of sulfur dioxide in the gas (Table. I) [6].

Table I

SO_2 oxidation technologies in sulfuric acid production

Process	SO_2 concentration, %	Conversion, %	SO_3 emission [2)]
PK/PA	3-6	97.5-98.5[4)]	0.4 kg/t MH*
DK/DA	6-12	99.6[1)]	0.1 kg/t MH
WCP Process	0.05-7	98.0	< 10 ppmv SO_3
Process based on NO_x	0.05-2	near 100[3)]	no data
Process based on H_2O_2		> 99.0	very low

[1)] – when burning sulfur, [2)] – SO_3 + H_2SO_4 expressed as SO_3, [3)] – possible emission of NO_x, [4)] – for the present factories conversion is 98%, * – monohydrate (100% sulfuric acid)

In Polish sulfuric acid installations one-stage PK/PA processes (single conversion/single absorption) and multi-stages DK/DA processes (double conversion/double absorption) are used [5].

PK/PA Technology

The process can be realized in new installations only when the process gas contains small amounts (3-6%) and changeable amounts of SO_2. Possible degree of conversion is about 98.5% and it can increase up to 99.1% in the case of using catalyst modified with cesium. In the factories that already operate it is very difficult to achieve conversion above 98%.

PK/PA technology is used in two Polish installations of metallurgic type (Huta Miedzi LEGNICA) and in one installation of sulfur type (GZNF FOSFORY). Despite the fact that all the installations are equipped with four-shelves converters, a possibility of obtaining high SO_2 conversion are kinetically limited and increase of load to the installation with gaseous SO_2 means increase of sulfur dioxide emission to atmosphere. Thus, the factories were additionally equipped with off gases desulfurization installations (Fig. 5, 6). In Linde solution (Fig. 5) selective physical absorption SO_2 in a solvent that can be regenerated is used. Stripped SO_2 enriches the process gas directed to sulfuric acid plant, stabilizing changes in SO_2 concentration and the operation of converter i.e. conversion of SO_2 to SO_3. In a factory of sulfur type alkali absorption of SO_2 was used with production of commercial sodium hydrogen sulfate (IV) (Fig. 6). Main Polish sulfuric acid factories indicators were listed in Table 2.

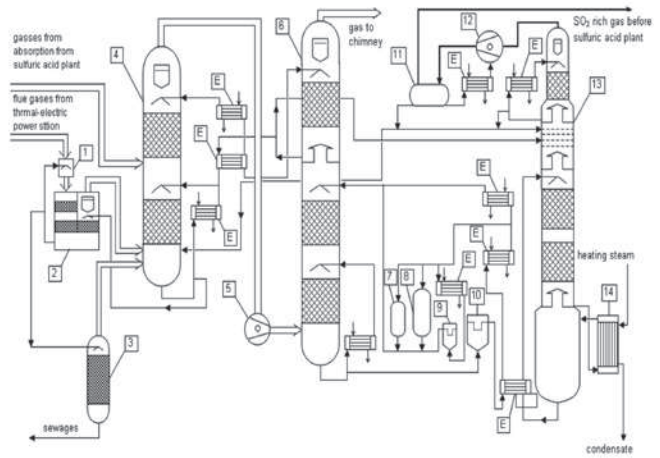

Fig. 5. Diagram of SOLINOX installation for SO_2 removal

Table 2

Sulfuric acid factories indicators for applied technologies

Index	Technology		
	PK/PA	DK/DA	TK/TA
Concentration of SO_2 in gas to converter, %	8	10	10-15
Linear gas flow, Nm/s	0.3	0.35	0.4
Converter diameter, m	6.5	5.2	4.4
Shelves system in a converter	4+0	3+1 or 3+2. 2+2	3+1+1 or 2+2+1
Catalyst consumption index, dm³/tMH·24h	200-280	170-200	160-180
Efficiency of oxidation process, %	95	99.5	99.95
Efficiency of absorption process, %	99.9	99.95	99.995
Emission of SO_2 + SO_3, kg/h	250	50	4
Number of absorption towers	1	2	3
Number of heat exchangers	4	5-6	7
Steam recovery index, t/tMH	1.8	1.5	1.3-1.5
Sulfur consumption index, kg/tMH	333	329	327

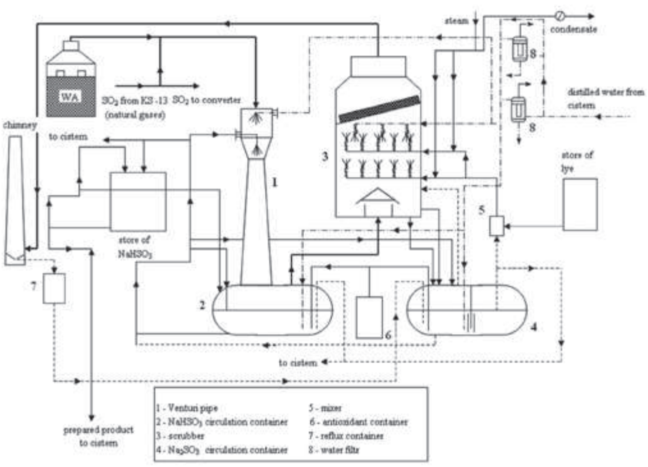

Fig. 6. Diagram of sodium hydrogen sulfate (IV) installation

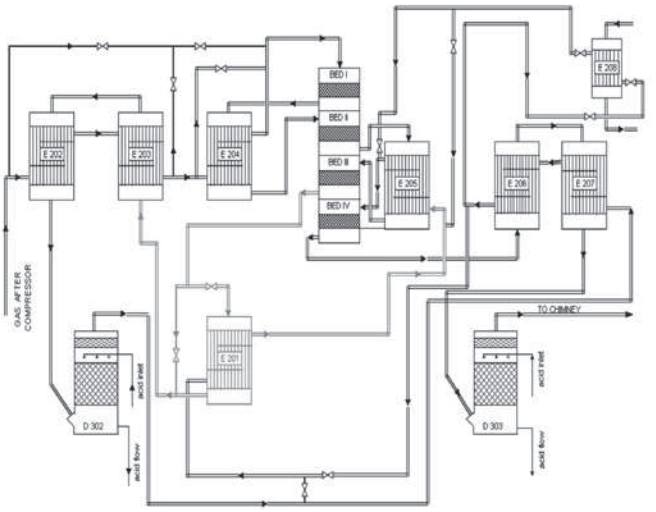

Fig. 7. Auto-thermal technological solution of converter-absorption installation for installation of metallurgical type

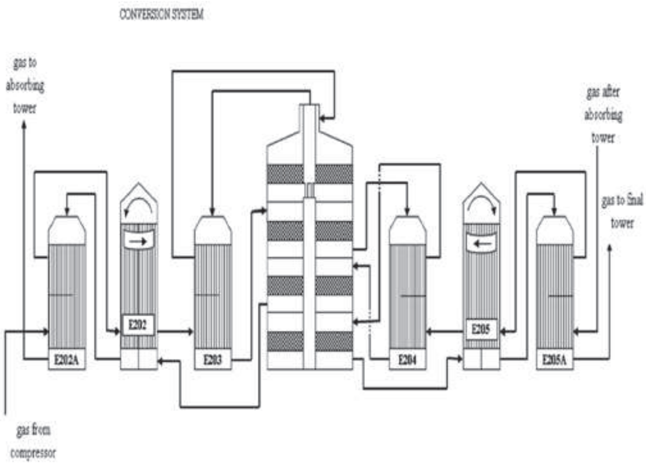

Fig. 8. Technological solution of converter-absorption installation in ZGH BOLESŁAW Bukowno installation

DK/DA Technology

DK/DA Technology should be realized when SO_2 concentration is higher than 6%. Efficiency of the first stage of oxidation should be about 95%. Absorption of SO_3 causes movement of SO_2 oxidation balance towards production of SO_3 and gives a chance to increase thermodynamic efficiency of the process to about 99.6%.

In the installations of sulfur type auto-thermal process at loads up to 6% SO_2 there are no problems with realization. Despite the fact that use of that technology in the installation of metallurgic type in an auto-thermal way was very difficult, due to high changeability of gas content and its flow as well as temperature, the problem has been solved successfully in Poland (Fig. 7). For the accepted idea of technological solution of converter-absorption installation, E201 exchanger transfers surplus heat from 1st conversion to warm up the gas directed to IV shelf of the converter – 2nd conversion.

Determination of operational parameters of the converter for given conditions of the process in the entire production cycle is a task of technologist who optimizes SO_2 oxidation process. During determination of those parameters, rules of quantitative realization of the process, of limitations associated with deactivation of catalyst as well as material and kinetic limitations, should be obligatory.

The above mentioned rules were used in designing of other sulfuric acid factories of metallurgic type, among others in BOLESŁAW Mining Metallurgical Plant in Bukowno, that operate in auto-thermal way (Fig. 8).

Oxidation of SO_2

At the beginning of 70's, in Poland pioneer research works were carried out on new type of low resistive vanadium catalysts having shape of Raschig rings and of different diameters with high catalytic activity, very good physical properties and low resistance coefficient [10]. The catalysts had ability of accumulation of greater amount of dust without increase of hydraulic resistance of the layer. Among other, technological solution that stabilizes texture and structure of the catalyst at the stage of its extrusion by use of a special stabilizer that at the same time has pores generation properties, was developed. Also the method of catalyst formation, using SO_2 produced in the result of oxidation of sulfur introduced to the catalyst at the stage of its production, has been developed. On the basis of kinetic test results and their operational verification, coefficients required for calculation of arrangement of low resistive catalyst in the converter and proper shelf mass surplus, when taking into consideration the process conditions, were developed.

Implementation of the catalyst gave huge economical and ecological benefits and made Polish sulfuric acid factories of metallurgical type the world leaders.

In BAT guidelines it is recommended to use on selected shelves the catalyst promoted with cesium, due to its more advantageous kinetic properties in the range of low temperatures. Use of catalyst of such a type enables increasing kinetic possibilities of SO_2 oxidation. The catalyst, due to its properties, is preferably used on the last shelf of the converter or as the initiating layer on I shelf, especially in the installations that convert the gas from metallurgical plants, using single conversion method. When using DK/DA technology benefits are not significant.

However, we have to remember that catalyst working in industrial conditions is deactivated, among others, under influence of corrosive iron that is introduced to the active part of the catalyst. The catalyst loses its properties and the cesium catalyst loses them faster than traditional catalyst.

Summary

In the process of gas purification, after roasting of non-ferrous metal ores, a solution recommended in BAT that guarantees high purity of the gas processed to sulfuric acid, is used, which enables extending production cycles under condition that the process is optimized.

The solutions used for absorption of water and sulfur trioxide do not differ from the standards determined by BAT and optimization of processes that is better than technology offered by BAT, guarantees very high and stable absorption effectiveness in the entire production cycle.

All Polish installations use DK/DA technology that is preferred by BAT or use accepted technology (PK/PA + final SO_2 absorption). Due to the developed solutions installation can operate auto-thermally.

Vanadium catalysts, selected adequately to the process conditions, are used according to the standards that are in force.

Optimization of installation's operational parameters, used in some factories, enables stabilizing emission of sulfur compounds to atmosphere, according to BAT requirements. Use of that technology is better than the solutions offered as BAT.

In the result of consequent modernization of sulfuric acid industry we can observe significant improvement of condition of the environment which is covered by emissions from those factories, what allows using the areas as farm land.

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