Process Application Report

On-line Concentration Determination of Sulfuric Acid

1. Introduction (reference [1], [2])

Sulfuric acid is a very important raw material in the chemical industry and is used in different chemical processes like:

- production of fertilizers
- production of phosphoric acid, hydrofluoric acid
- synthesis for the production of sulfonates and sulfates (dyes, softeners, tensides, explosives, fibers, pharmaceutical products, plastics etc.)
- production of artificial silk and viscose
- production of titanium oxide (paint industry)
- production of sodium sulfate (glass industry and detergent production) and aluminum sulfate
- battery acids
- desiccants
- pickling baths in steel industry.

The chemical formula of sulfuric acid is H_2SO_4.
100 % sulfuric acid is a color- and odorless oily liquid with a very strong hygroscopic action. Sulfuric acid is miscible with water in any ratio, however the dilution process has to be performed with extreme caution as a large amount of heat is generated during this procedure.

Sulfuric acid and oleum in particular quickly destroy all kinds of tissue and fabric on contact.

Today the most important industrial process for the production of sulfuric acid is the so called "double contact process". H_2SO_4 is produced by dissolving sulfur trioxide (SO_3) in concentrated sulfuric acid, followed by dilution with water, to get the desired concentration. For the control of the H_2SO_4 production and dilution process an on-line measurement of the sulfuric acid concentration is necessary.

2. Concentration determination of sulfuric acid

The concentration of aqueous solutions of sulfuric acid is quoted as % w/w H_2SO_4.
Figure 1 shows the density/concentration and sound velocity/concentration relationship for sulfuric acid at 40 °C. The diagram for 20 °C is very similar, except for the smaller measuring range (oleum with a content of more than 20% free SO_3 is solid at 20 °C).

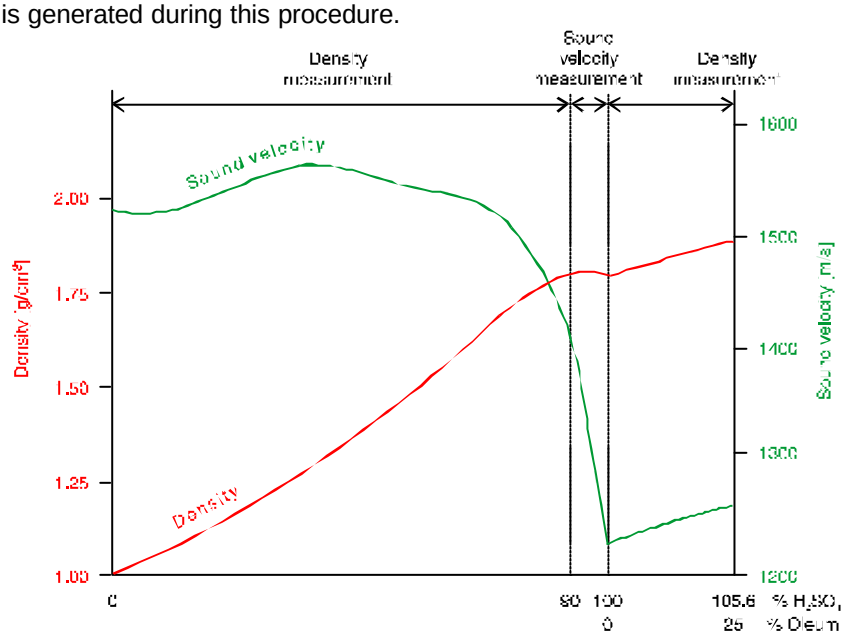

Fig. 1: Density and sound velocity of sulfuric acid and oleum at 40 °C.

The concentration of oleum of different strength is quoted according to the content of "free SO_3" in 100 % sulfuric acid; thus oleum-40 contains 40 % of free SO_3 in 100 % sulfuric acid (this corresponds to an equivalent concentration of 109 % H_2SO_4 as the result of a titration).

% free SO_3	Equivalent % H_2SO_4
0	100.00
10	102.25
20	104.50
30	106.75
40	109.00
50	111.25
60	113.50
70	115.75

To achieve highest accuracy, the physical property (density or sound velocity) which shows the biggest change upon change in sulfuric acid concentration should be employed for the determination of % H_2SO_4.

Density measurement should be used to calculate H_2SO_4 concentration from **0 to 90 % w/w**, because density has a steep and almost linear dependence on the acid concentration.
Sound velocity should be used to determine the H_2SO_4 concentration in the range of **90 to 100 % w/w**, since it is strongly influenced by a concentration change whereas density changes only very little in this range. In the oleum range from 0 to 25 % free SO_3, density measurement should be utilized again to calculate the H_2SO_4 concentration.

Anton Paar produces instruments for the laboratory and on-line measurement of density and sound velocity of H_2SO_4 and oleum.

The **DSA 48 Sulfuric Acid Analyzer** is a laboratory instrument that measures density and sound velocity simultaneously. Depending on the concentration range the density or sound velocity result is employed for the determination of % w/w H_2SO_4.

Anton Paar on-line transducers **DPRn** and **SPRn** offer the possibility of an accurate concentration determination of H_2SO_4 and oleum for process control.

3. Measuring principles

3.1 The DPRn density transducer

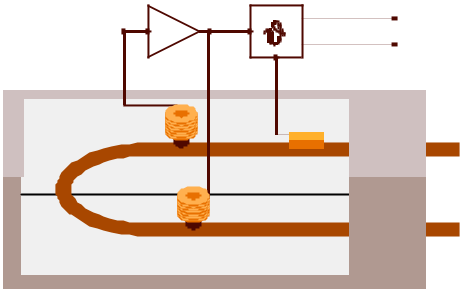

Fig. 2: DPRn density transducer

Figure 2 illustrates the principle of density measurement. The U-tube, a mechanical oscillator system, is excited. It is kept oscillating at its resonant frequency by two coils and an electronic circuit. Oscillation period and sample temperature are measured and transferred to an evaluation unit for data processing and control purposes.

The accuracy of DPRn density transducers typically amounts to ± 1 x 10^{-4} g/cm^3.

3.2 The SPRn sound velocity transducer

Sound velocity is measured with an SPRn sound velocity transducer as shown in fig. 3.

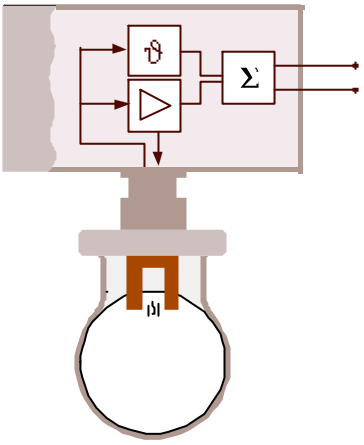

Fig. 3: SPRn sound velocity transducer

The active parts of the SPRn consist of an ultrasonic transmitter and receiver.
The electronics measures the propagation time of the ultrasonic pulses through the sample. By knowing the

distance between the transmitter and receiver and the propagation time, sound velocity can be calculated. Since the sound velocity is highly temperature dependent, a temperature sensor is also built in. Sound velocity and temperature information is transferred to an evaluation unit to convert the measured sound velocity into concentration units.

4. Typical installation sites

4.1 Double contact process

In figure 4 a simplified scheme of the "double contact process" is shown [3].

The starting material for the production of sulfuric acid is sulfur dioxide (SO_2), which is produced by combustion of sulfur or roasting of sulfur containing ores.

Sulfur dioxide is reacted with oxygen (oxidized) to give sulfur trioxide. This reaction occurs at four to five vanadium oxide contacts. After the third contact most of the formed SO_3 is removed from the reaction mixture and fed into the first absorber. The residual reaction components (SO_2 and O_2) are again reacted at the vanadium oxide contacts. The formed SO_3 is fed into the second absorber.
In the "double contact process" a total SO_2 conversion of 99.6 to 99.7% is reached.

In the intermediate and final absorbers sulfur trioxide is dissolved in 98 % to 100 % sulfuric acid to give *fuming sulfuric acid or oleum* (fuming: escaping sulfur trioxide forms fumes of sulfuric acid with atmospheric humidity). The oleum or concentrated sulfuric acid is diluted to the desired concentration.

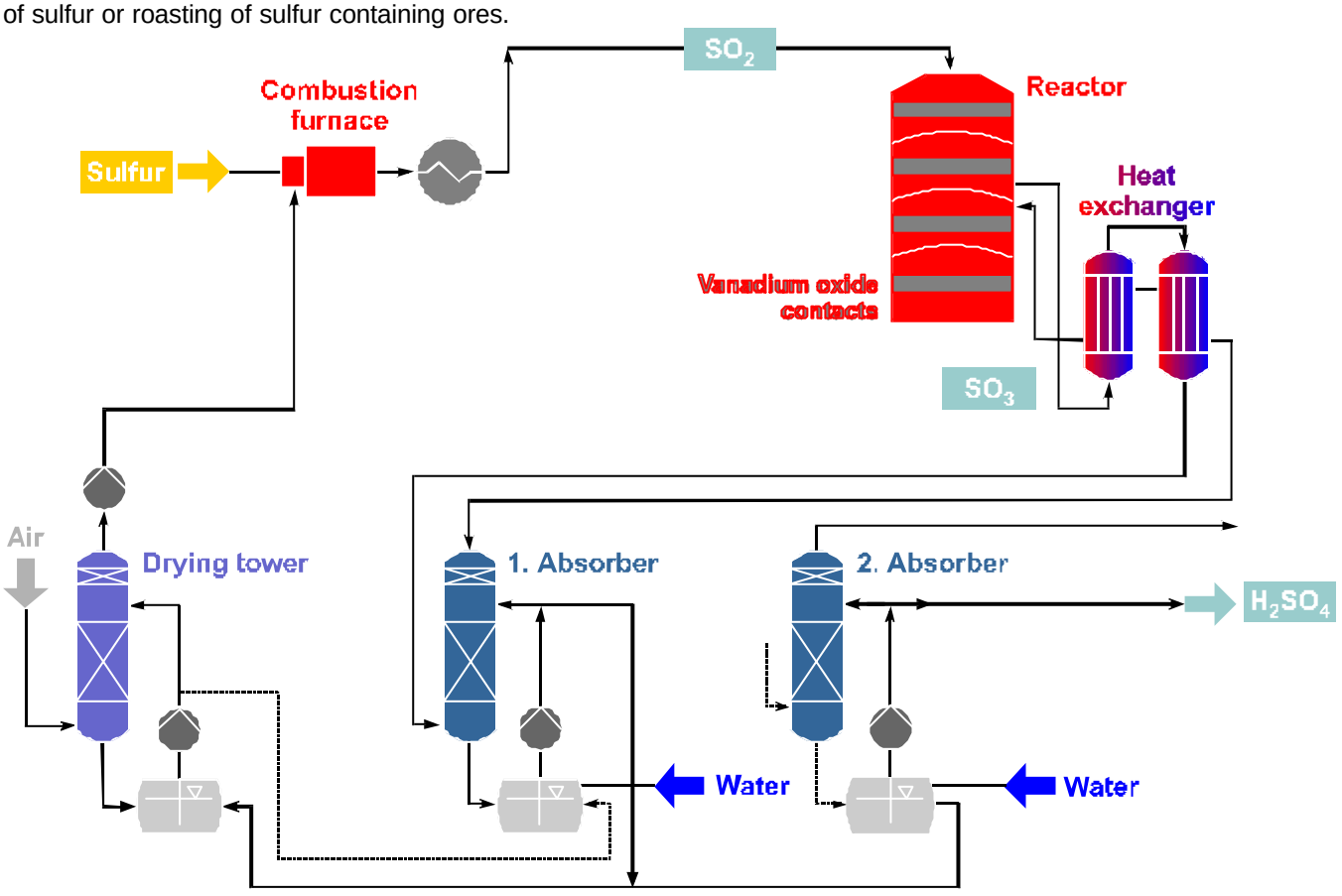

Fig. 4: Simplified scheme of the "double contact process"

4.2 On-line measurement of H_2SO_4 concentration

Depending on the requirements the density and/or sound velocity transducers can be installed at different sites in the process.

At any installation site where the expected H_2SO_4 concentration is in the range of 0 to 90 % w/w a DPRn density transducer can be mounted in a bypass. For this application the DPRn transducer must be made of tantalum which shows an excellent resistance against sulfuric acid. For the measurement of oleum the DPRn transducer must be made of glass.

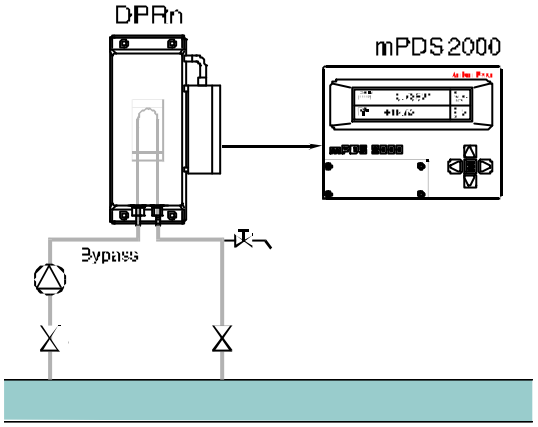

Fig. 5: Bypass installation of the DPRn

For H_2SO_4 concentration in the range of 90 to 100 **%** w/w a gold plated SPRn sound velocity transducer is used. The gold plated SPRn transducer is inserted into the line using standard fittings (DIN 2633, DN40 PN16). All wetted parts of the transducer are gold plated to prevent corrosion of the transducer material by sulfuric acid.

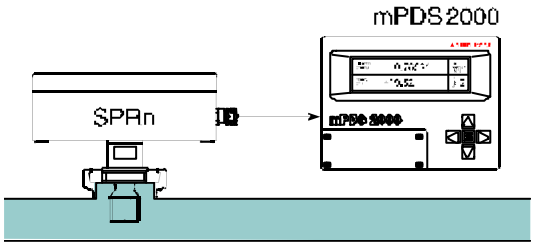

Fig. 6: In-line installation of the SPRn

Density or sound velocity and temperature are transferred to the mPDS 2000 by a two wire cable. The same cable powers the transducer and it can be of almost any length.

5. Measuring range

DPRn transducer:
Temperature: 0 to 100 °C
Concentration: 0 to 90 % w/w H_2SO_4
0 to 25 % oleum

SPRn transducer:
Temperature: 20 to 50 °C
Concentration: 90 to 100 % w/w H_2SO_4

6. Measuring results - accuracy

Following parameters influence the measuring result:

- **Density** accuracy: 1 x 10^{-4} g/cm3
  Corresponding variations in H_2SO_4 concentration: < 0.05 % w/w H_2SO_4 or oleum (typical)
- **Sound velocity** accuracy: 0.1 m/s
  Corresponding variations in H_2SO_4 concentration: < 0.05 % w/w H_2SO_4 (typical).
- **Temperature** influences are compensated by the built-in temperature measurement.

? **Total error:**
Variations of all process conditions occurring in practice lead to a total error of <0.1% w/w H_2SO_4.

7. Benefits

- Anton Paar on-line transducers guarantee **highly accurate** density and sound velocity measurement of H_2SO_4 and oleum.
- The concentration of H_2SO_4 and oleum is determined over a **wide concentration range**.
- DPRn and SPRn transducers allow measurements to be automatically converted into % H_2SO_4 by the mPDS 2000 evaluation unit.
- H_2SO_4 quality is continuously assured during the production process.

- Anton Paar sound velocity transducers offer the possibility to measure in the concentration range of 90 to 100 % w/w H_2SO_4 which is of particular interest during the production process.
  In contrast conductivity measurement cannot be used to determine %w/w H_2SO_4 in this concentration range.
- During the dilution process of concentrated H_2SO_4 or oleum the H_2SO_4 concentration can be monitored and the production yield can be improved.

Anton Paar on-line transducers are successfully used at:

DONAU-CHEMIE AG, Austria
CU-CHEMIE UETIKON; Switzerland
HAYS CHEMICALS, United Kingdom
BORREGAARD INDUSTRIES Ltd., Norway
and many others.

8. Summary

On-line density and sound velocity measurements provide accurate % w/w H_2SO_4 determination at important stages of the production process of sulfuric acid.
The applied measuring methods are simple, rigid and accurate.

9. References

[1] Chem. unserer Zeit, 1982, 16, 149-159
[2] Ullmann's Encyclopedia of Industrial Chemistry, (4.), 21, 117-166
[3] Römpp Chemielexikon, Georg Thieme Verlag, 9.Auflage, 1989

For further information please contact:

B-R Controls Pty Ltd
3/95 Hunter Street
HORNSBY NSW 2077

Tel: +61 2 9476 2133
Fax: +61 2 9476 2688
Email: mail@brcontrols.com.au