

# Guideline

## on handling hydrogen in sulfuric acid producing plants

### introduction

In large-scale sulfuric acid plants (see [1]), hydrogen formation is always to be expected as a result of surface (metallic) corrosion. The hydrogen that is formed can then, under certain circumstances, lead to a hazardous explosive atmosphere (geA) when combined with oxygen.

In these guidelines, the formation of hydrogen is explained in a simplified manner and the boundary conditions that can lead to a dangerous, potentially explosive atmosphere are shown. Based on this, scenarios and measures are described to avoid such system events. This does not release the system operator from carrying out an individual safety assessment in order to reflect the special circumstances of the individual case. In this respect, the options for action described here can and should always only be possible variants of the procedure.

The guidelines presented here exclusively address questions of plant safety due to the formation of a dangerous, explosive atmosphere from the formation of hydrogen through metal corrosion. Further considerations that result from the material removal and any questions that may have to be asked about the stability of the system are not discussed.

### 1. Hydrogen formation

During the corrosion by the sulfuric acid, the metal is oxidized, corresponding metal sulphates and hydrogen are formed.

Exemplary for iron (steel):  $\text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2$

In the case of sulfuric acid, there is usually extensive corrosion erosion. The removal rate is given in mm/year, based on an area of one m<sup>2</sup>. For example, 1 mm/(m<sup>2</sup> and year) for iron (Fe) corresponds to a hydrogen quantity of 3.2 Nm<sup>3</sup>/(m<sup>2</sup> and year).

That is, for a fictitious metallic surface (heat exchanger) of 800 m<sup>2</sup> with a corrosion rate of 0.1 mm/year (technically stable) and 8,000 operating hours/year, this would correspond to a hydrogen volume of 0.032 Nm<sup>3</sup>/h. The amounts of hydrogen are similar for other metals (see [3]).

The following figure shows the corrosion rates for two steels as a function of the sulfuric acid concentration and the acid temperature.

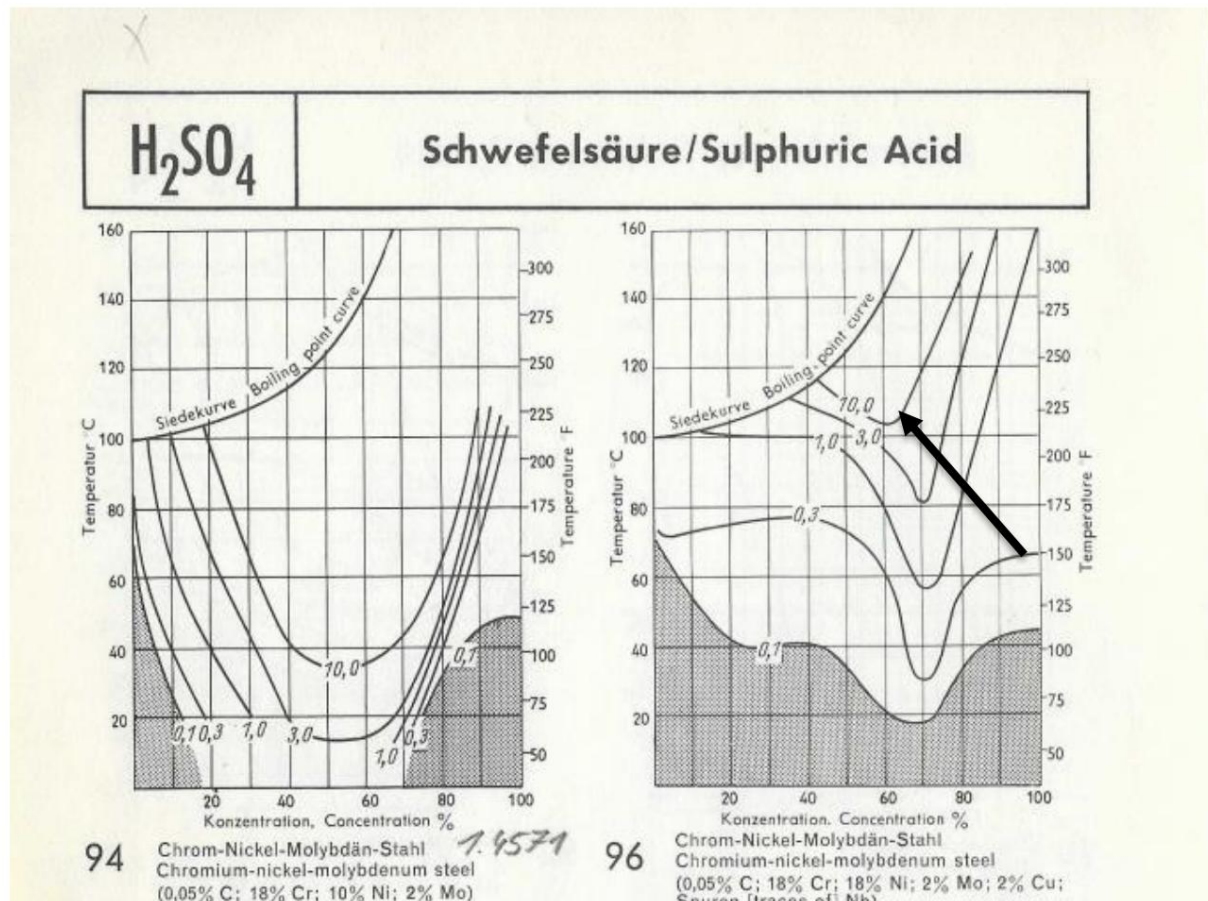


Fig. 1: Corrosion rates as a function of temperature and sulfuric acid concentration, see [2]

You can clearly see the dependency on the material, the temperature and the acid concentration. In principle, the influence of the flow velocity must also be taken into account with steels (e.g. carbon steel) (see [1]). Higher H<sub>2</sub> formation rates are to be expected for (metal) surfaces in contact with the flow.

In order to better illustrate the influence of water ingress and temperature, the following example 1 is described (see arrow in Fig. 1, Diagram 96):

- a) Normal operation: An intermediate absorber is operated at an acid concentration of approx. 98.5%, a temperature of approx. 65 °C and has a wetted metal surface of 800 m<sup>2</sup>. According to Fig. 1 or Diagram 96, there is a removal rate of 0.3 mm/year and thus a hydrogen formation of approx. 0.1 Nm<sup>3</sup>/h.
- b) Too much water: Due to the dilution and the associated insufficient cooling, the temperature rises to 105 °C, for example, and the concentration drops to 63 %  $\ddot{y}$  this increases the corrosion rate by a factor of 30 and the formation of hydrogen from approx. 0.1 Nm<sup>3</sup>/h to approx. 3 Nm<sup>3</sup>/h.

If one assumes that suitable materials (see [1] Chapter 4.14) were used in the design of the plant and that corresponding design principles were applied, the main cause of hydrogen formation, in addition to insufficient cooling, is the uncontrolled, unregulated entry of water into the plant or into the sulfuric acid due to corrosion of the plant steel.

The following water sources usually come into consideration:

- (1) Process water to maintain concentration
- (2) Leaks in the water cooling of the absorbers
- (3) Leak in waste heat system
- (4) Humidity (especially during system downtimes, maintenance shutdowns, etc.)
- (5) Improper cleaning and rinsing measures, leaky shut-off valves
- (6) Leakage from other steam or water systems

These must be controlled or avoided with suitable measures.

## 2. Boundary conditions

When a hazardous explosive atmosphere is ignited, hydrogen reacts with oxygen in a highly exothermic reaction to form water (see [3]).



The ignition energy required for this depends on the gas composition and the pressure, but is low. Thus, the ignition of a corresponding mixture in the explosive area is possible.

The explosion limits LEL (“lower explosion limit”) and UEL (“upper explosion limit”) depend on the temperature and the gas composition (see [3]).

At room temperature, the LEL is 3.8 mol% H<sub>2</sub> in air and 3.6 mol% H<sub>2</sub> in a mixture of 40% N<sub>2</sub> plus air. At a temperature of 400 °C, the lower limit falls to 1.5 mol% H<sub>2</sub> in air.

## 2.1 Normal operation of the production facility

Normal operation here means that the plant is producing and all parameters are in the target range (example 1 a)). In example 1 b) the deviation is that too much water would get into the intermediate absorber without there being a fault (see Chapter 3.1).

According to 1 a), the hydrogen formation rate is 0.1 Nm<sup>3</sup>/h.

According to 1 b), the hydrogen formation rate is 3 Nm<sup>3</sup>/h.

With a gas throughput of 50,000 Nm<sup>3</sup>/h, this corresponds to a molar H<sub>2</sub> concentration of 2 ppm or 60 ppm. Since the LEL is in the percentage range (>10,000 ppm corresponds to >1% by volume or >1 mol%), geA can be ruled out in this example. Nevertheless, a corrosion rate of 10 mm/year is essential for (steel) wear and quality reasons be avoided.

## 2.2 Plant Downtime

Plant standstill is understood here to mean that the production plant is not producing (maintenance, malfunction, etc.) and the gas throughput is stopped. In principle, hydrogen accumulation can take place if one of the faults described under 3.1 occurs.

To illustrate the influence of time on the accumulation Example 2:

The intermediate absorber described in Example 1 has a gas space of 200 m<sup>3</sup>, the gas space is filled with air (dried or moist) due to the shutdown of the plant. As described in Example 1, the hydrogen formation rates are 0.1 and 3 Nm<sup>3</sup>/h. The hydrogen may accumulate in the head of the absorber.



- a) Daily shut-off, 8 hours: Hydrogen concentrations of about 0.4 mol % in example 1a) and 12 mol % in example 1b) will be established. The 12 mol% are above the LEL, a geA is present.
  
- b) Revision shutdown, longer than 120 hours: If no appropriate measures are taken and take effect to reduce hydrogen formation and / or prevent accumulation, the LEL is safely exceeded and the hazardous area is entered.

### 3. Countermeasures

In order to avoid a geA, two essential aspects should be considered. How do you prevent or reduce

- 1. the formation of hydrogen  
and
- 2. the accumulation within the plant.

Suitable countermeasures can result from the following areas:

- (1) Apparatedesign
- (2) Operation of the facilities
- (3) Repair and maintenance of the facilities

### 3.1 Malfunction / Countermeasure

disturbance	Possible Cause	detectability	Possible countermeasures	comment
On the fly, uncontrolled entry from process water into the absorbers and pump templates	faulty Concentration measurement: <ul style="list-style-type: none"> <li>• Defective measuring device</li> <li>• not flowed through Messarmatur</li> <li>• defective Control armatur</li> </ul>	Not immediately recognizable.  Increased or unusually high process water addition	redundancy of concentration measurement <ul style="list-style-type: none"> <li>• 2 times continuously</li> <li>• 1 time continuously and Once discontinuously (e.g. sampling and concentration determination every 6 hours)</li> <li>• Flow monitoring</li> <li>• Additional possibly automated shut-off valve</li> </ul>	cross-check at Measured value deviation of the redundant concentration determination
When the plant is at a standstill, more uncontrolled entry from process water into the absorbers and pump templates	Leaking or incorrectly opened control fitting for process water	Not immediately recognizable, since there is usually no flow through the concentration measurement and overlaying of different concentrations is possible when the absorber pumps are switched off	Locking of the central Process water access to System with shut-off valves (Open/Close) and/or blind washer	It should be specified that in Plant downtime always the central one process water access is closed, e.g. in a "block and bleed" arrangement

disturbance	Possible Cause	detectability	Possible countermeasures	comment
<p>With cooling water cooled absorbers on the fly, uncontrolled entry from process water into the absorbers and pump templates</p>	defective heat exchanger, leakage	waste the Acid concentration, atypical decrease in the regulated process water volume	<p>The pressure conditions constructively so that there is always acid in the cooling water comes and not vice versa.</p> <p>At least that total cooling water return by means of a conductivity/pH measurement in order to detect and alarm a leak</p>	
<p>With cooling water cooled absorbers in the plant standstill, more uncontrolled entry from process water into the absorbers and pump templates</p>	defective heat exchanger, leakage	<p>Not immediately recognizable, since there is usually no flow through the concentration measurement and overlaying of different concentrations is possible when the absorber pumps are switched off</p>	<p>Switch off the cooling water, ie depressurize it, if necessary empty the WT on the cooling water side, if possible do not switch off the absorption circuits in order to maintain the pressure conditions</p>	In winter operation is consider the possibility of freezing.
uncontrolled entry of water /	<ul style="list-style-type: none"> <li>Defects heat exchanger / leakage in</li> </ul>	<ul style="list-style-type: none"> <li>Formation of hot acid condensate in gas flow</li> </ul>	<ul style="list-style-type: none"> <li>Monitoring the humidity in the process gas</li> <li>Regular checking of the condensate drains, the</li> </ul>	Around apparatuses and Heat exchanger in which the hot

disturbance	Possible Cause	detectability	Possible countermeasures	comment
steam in the process gas space	<p>steam system on the process gas side</p> <ul style="list-style-type: none"> <li>• Moisture in sulfur</li> <li>• Insufficient drying the process gases or combustion air</li> <li>• Boiler damage on steam system</li> </ul>	<ul style="list-style-type: none"> <li>• Waste of Acid concentration, atypical decrease in the regulated Amount of process water in the absorption</li> <li>• clearly visible Exhaust plume on the chimney</li> </ul>	<p>sight glasses in the absorbers over the Filter candles and the Chimney flag during plant tour</p> <ul style="list-style-type: none"> <li>• Alerting the minimum acid concentration</li> <li>• Synchronism monitoring feed water/steam delivery</li> </ul>	<p>acid condensate accrues, these should be replaced by suitable choice of material to be protected.</p> <p>Appropriate Review / Maintenance particularly vulnerable plant parts Revisionsabstellungen</p>
<p>Access from Humidity during longer plant downtimes, repair and inspection shutdowns, catalyst replacement, etc. by opening the Apparatus, forced ventilation, drafts, etc.</p>	<p>Formation of "dilute acid" on the gas side inner walls of apparatuses</p>	<ul style="list-style-type: none"> <li>• Previously dry Surfaces in the gas system begin to get wet.</li> <li>• In horizontal Gas lines can change collect liquid</li> </ul>	<ul style="list-style-type: none"> <li>• Monitoring of the hydrogen concentration, ie measurement at regular intervals at the highest points of the areas at risk.</li> <li>• Opening the apparatus at the highest points so that the hydrogen formed can evaporate and does not accumulate.</li> </ul>	<p>If possible, the manholes and inspection openings should always be covered to prevent moisture from entering.</p> <p>where applicable special measures such as inerting for individual devices</p>



disturbance	Possible Cause	detectability	Possible countermeasures	comment
				set one or continues to operate absorber in order to do so for certain  System sections to avoid the entry of humidity.
improper cleaning and Flushing measures, leaking shut-off valves	Rinse with water from acid lines, process gas lines heat exchangers or Apparatus prior to dismantling or for the purpose of cleaning of deposits  This leads to uncontrolled "dilute acid formation"	Not immediately recognizable	<ul style="list-style-type: none"> <li>• Usually no rinsing with water in the system</li> <li>• Drain acid-carrying systems before dismantling, blow out if possible</li> <li>• Under effective Dismantle protective measures without rinsing</li> <li>• Flush in a safe place when dismantled</li> <li>• Blind or blind devices for unavoidable cleaning and rinsing measures. secure separate.</li> </ul>	<ul style="list-style-type: none"> <li>• Carry out measures quickly.</li> <li>• Systems where possible blow dry</li> </ul>

### 3.2 Measurement Method

The information provided here is for guidance only. In particular, the measuring ranges can vary depending on the provider of the application. The specific process conditions such as temperature and contamination are also decisive for the selection of a measuring method. Measuring ranges can often be adapted to the individual measuring task through skillful parameterization adjust.

measurement method	metric	concentration Area	advantages	disadvantage	Remarks
acid and oleum concentration (in % H <sub>2</sub> SO <sub>4</sub> )	conductivity	0 – <100 %	Low cost	<ul style="list-style-type: none"> <li>• Uncertain measuring range between 80% and 95 %.</li> <li>• Multiple Concentrations have the same conductivity</li> <li>• Correlation of conductivity and Temperature not linear</li> </ul>	<ul style="list-style-type: none"> <li>• Applications over a large concentration range only possible with non-linear temperature compensation.</li> <li>• Not suitable for changing ionic accompanying substances concentration</li> </ul>
	Ultrasonic	80-100% and 110 – 120 %	Clear signal, low-maintenance, long-term accuracy	Relatively high cost	density – sound – Combination devices for use in the acid / oleum area
	density	0 – 90% and 100 – 110 %	Clear signal	Relatively high costs, recurring calibration and maintenance effort	

measurement method	metric	concentration range	advantages	disadvantage	Remarks
	Refractive index	0 – 75% and 95 – 110 %	Clear signal	Less suitable for org. Contaminants or free gases containing acids	
water in process gas	wavelength (Laser-Signal) A Lines spectroscopy	50 – 50000 ppm in-situ	measurement, low maintenance, hardly any Querempfindlichkeiten	High cost, relatively high instrumentation effort	Suitable for high gas temperatures up to 1500 °C
hydrogen in process gas	heat tone	0 – 10%  0,4 – 5 % (10 – 125% LEL) in gas mixtures	Easy to use, low cost	cross sensitivity with hydrocarbons and carbon monoxide (CO)	
Acid leaks in cooling water etc.	conductivity	0 – 500 $\mu\text{S}/\text{cm}$ 200 - 1000 $\mu\text{S}/\text{cm}$	Low cost, low maintenance		

### 3.3 Tank camp

When operating tank farms, especially sulfuric acid and oleum tanks made of metallic materials, these should be designed in such a way that the hydrogen formed cannot accumulate. Therefore, this should be discharged safely at the highest point of the tank, avoiding dead spaces via ventilation.

Larger tanks for technical sulfuric acids in the concentration range of 96% to 100% and oleum in the concentration range of 24% to 32% (up to 100% SO<sub>3</sub>) and a storage temperature of less than 40 °C are usually made of "normal steel".

Therefore, both the temperature and the concentration of the sulfuric acid/oleum and their quality (secondary components) are monitored.

The ventilation is usually designed in such a way that no moisture gets into the tank space (e.g. when defuelling) to reduce corrosion. For sulfuric acid tanks, this can be achieved by overlaying it with a dry gas (air, nitrogen, process gas from the final absorber, etc.).

Oscillating gases from oleum tanks are dried or cleaned by absorption.

The phase boundaries between liquid and gas phase are exceptions to the surface corrosion erosion. Higher rates of corrosion can occur in tanks that are operated at the same level for long periods of time and in submerged tank necks where gas bubbles collect.

For storage for tank inspection, the provisions in Chap. 3.1 measures for longer plant shutdowns, repair and inspection shutdowns as well as improper cleaning and flushing measures.

## 4. Bibliography

- [1] Winnacker - Küchler, Chemical Technology, Volume 3 Inorganic Basic Materials, Intermediates, Chapter 4 Sulfuric Acid, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005
- [2] Frank F. Berg, Corrosion Diagrams, VDI-Verlag GmbH, Düsseldorf, 1965
- [3] Hydrogen Safety Committee, Hydrogen explosions on the rise, Sulphur 355, November – December 2014, [www.sulphurmagazine.com](http://www.sulphurmagazine.com)