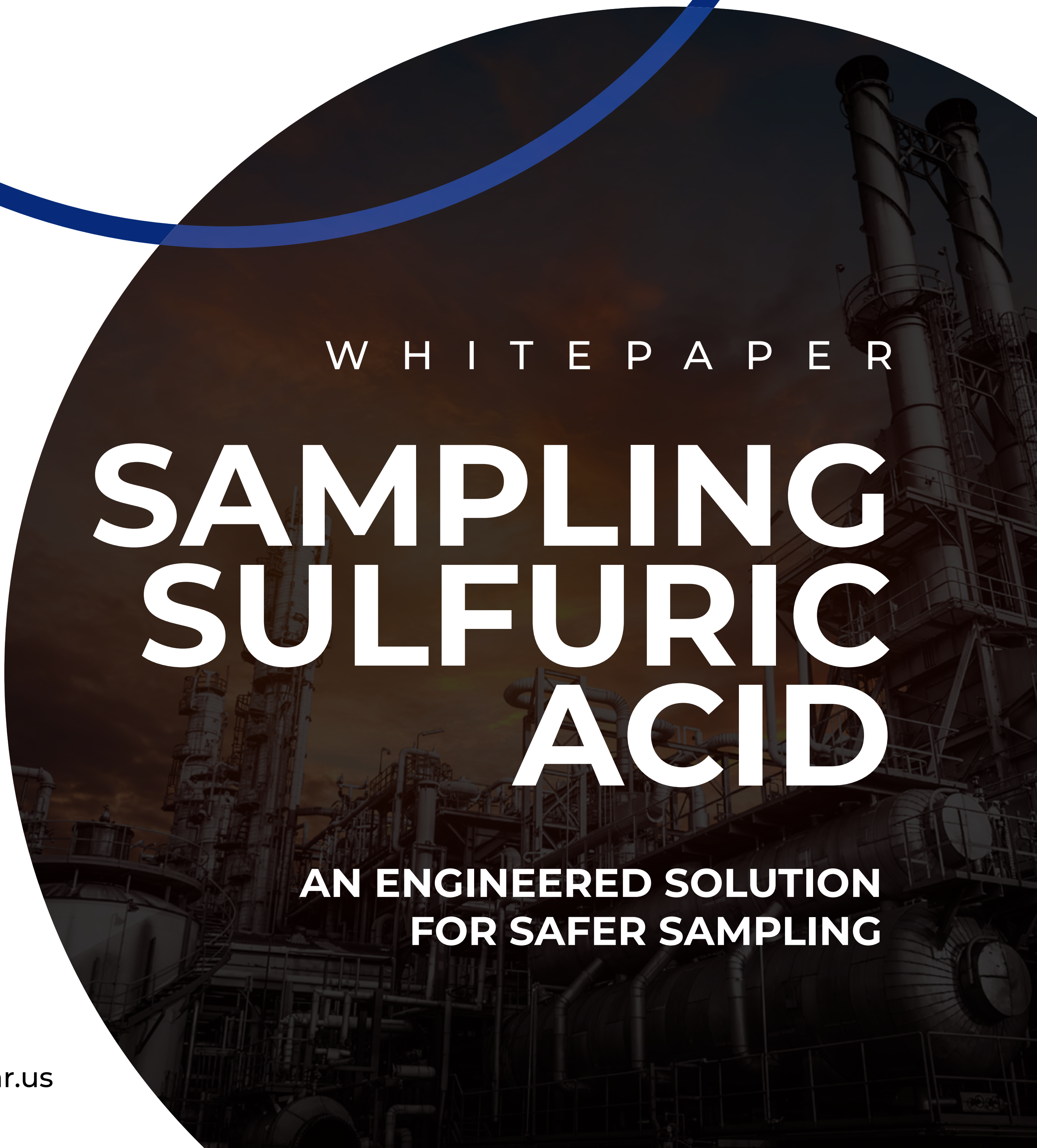
BIAR Sampling Systems



WHITEPAPER

SAMPLING SULFURIC ACID

AN ENGINEERED SOLUTION FOR SAFER SAMPLING

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Abstract

The primary aim of this document is to discuss how engineering controls are the most effective way to prevent accidental releases or injuries when sampling hazardous chemicals such as sulfuric acid.

We also discuss how sample system design is a key factor not only in improving safety, industrial hygiene and quality, but in creating an inherently safer sampling process. We can also see other benefits, such as reducing waste, improving efficiency and improving compliance with federal regulations. These are factors which influence day to day running costs and a plant's bottom line. We must bear in mind that sample stations are high risk locations where personnel run a higher risk of exposure to hazardous material. Where the risks of accidental releases are greater, it's in everyone's interest to ensure that the potential for chemical releases and accidents are kept to an absolute minimum, if not eradicated entirely. This article will be of interest to those that work with sulfuric acid and are interested in engineered solutions for reducing the exposure risk in the sampling process. It may also be of interest to those conducting PHAs', HAZOPs, Safety Audits, those involved in Process Safety Management and Continuous Improvement. As sulfuric acid is such a ubiquitous and vital component of the chemical industry, we need to utilize engineered solutions to protect workers and the environment from chemical releases.

The Chemical: Sulfuric Acid

Sulfuric acid (H_2SO_4) is an oily, colorless and odorless liquid composed of sulfur, hydrogen and oxygen also known as hydrogen sulfate, oil of vitriol, or sulphuric acid.

With a melting point of 10°C and a very high boiling point of just under 300° C, it reacts violently with water, organic and inorganic materials and can generate intense heat. Highly corrosive to certain metals, it will also cause severe burns when in contact with eyes or skin and its vapors irritate the respiratory tract. Severe exposure can result in fatality.

Sulfuric acid is the most important chemical in the industry today, and by a large margin, the most consumed and produced chemical in the world. This is because sulfuric acid is a vital raw material for countless chemical products and processes. A large proportion of sulfuric acid is used to make phosphoric acid, and when reacted with ammonia, it produces ammonia sulfate. Both phosphoric acid and ammonia sulfate are key fertilizers in the agricultural industry. Concentrated sulfuric acid (93-98%) is used to manufacture detergents, explosives, dyes, and petroleum products. It also has an important function as a catalyst in the alkylation process in refineries, where light olefins such as propylene, butylene, amylene, and fresh isobutane are reacted to produce higher octane gasoline.

Hazardous Substance

Unfortunately, accidents and releases involving sulfuric acid are quite common.

In a study conducted by Aryana F. Anderson, who worked in the Agency for Toxic Substances and Disease Registry at the CDC[1], sulfuric acid was ranked in the top five dangerous chemicals by incident in nine states. The nine states examined were: Colorado, Iowa, Minnesota, New York, North Carolina, Oregon, Texas, Washington, and Wisconsin during the period 1998-2008. Some interesting statistics regarding accidents and releases involving sulfuric acid are evident from the study:

- The highest percentage **(30%)** of injuries related to sulfuric acid were in the manufacturing sector.
- A high proportion of those injured **(74%)** were employees.
- Most of the injuries reported were burns.
- **41%** of sulfuric acid releases were the result of equipment failure, while **34%** were the result of human error, together a staggering **75%!**

1 Swift, Moore, Rose-Glowacki, & Sanchez, 2019)

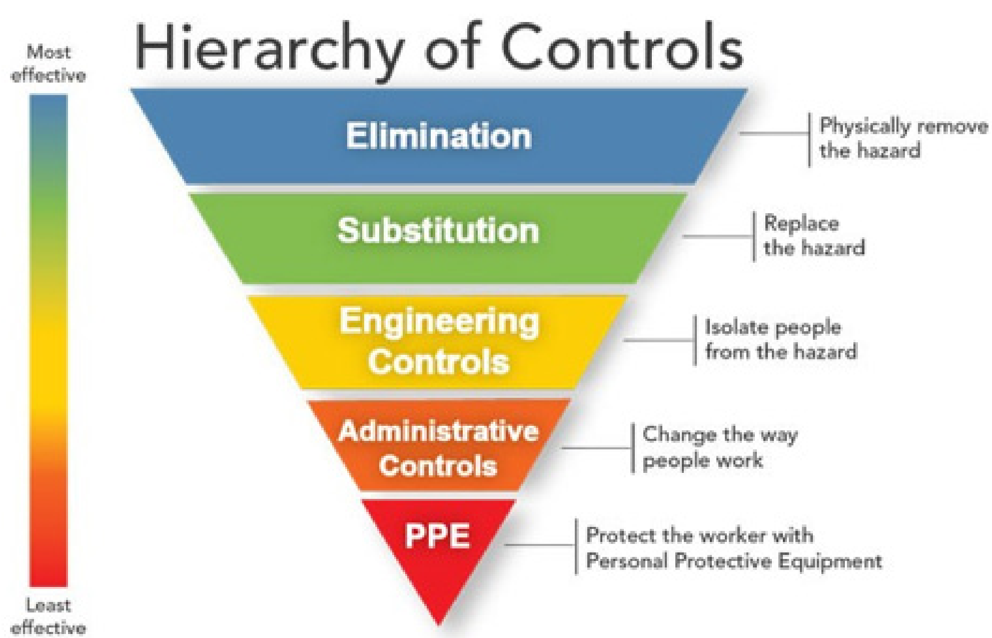
Mitigating Risk in the Sampling Process

How can we reduce the risk of employee exposure and chemical releases during the sampling process?

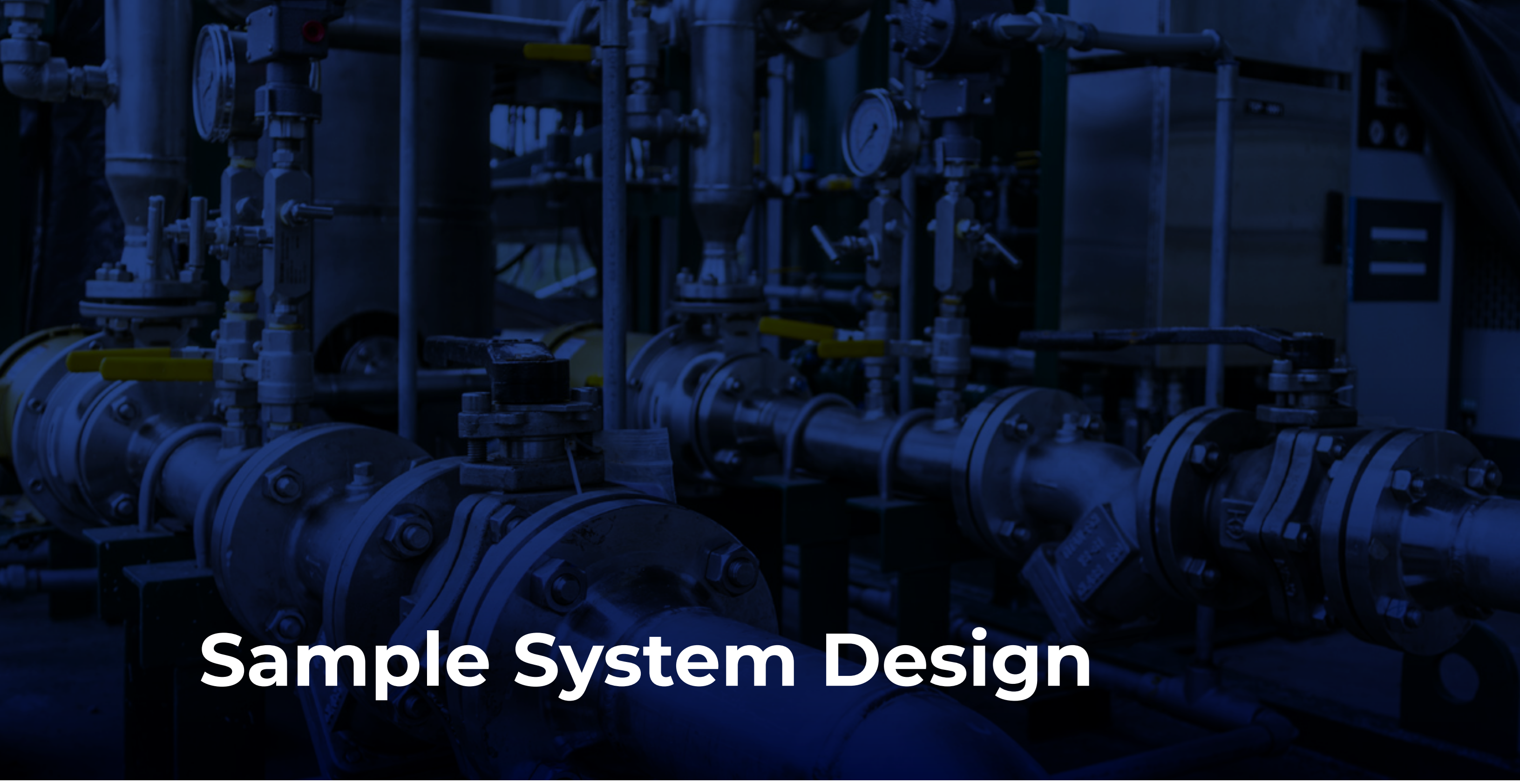
If we consider the Hierarchy of Controls below, we see that the most effective ways are to either eliminate sulfuric acid completely from the process or substitute it with another chemical. As sulfuric acid is such an important raw material, and in some cases a safer alternative, (eg. as a substitute for HF in the alkylation process) substitution and elimination are impractical. The most effective way to mitigate risks associated with sulfuric acid is to isolate people from the hazard using engineering controls. Engineering controls are more effective than either administrative controls or PPE, as they remove or greatly reduce the risk at source.[2]

> **ENGINEERING CONTROLS ARE MORE EFFECTIVE THAN EITHER ADMINISTRATIVE CONTROLS OR PPE, AS THEY REMOVE OR GREATLY REDUCE THE RISK AT SOURCE.**
>
> **- NIOSH**

Hierarchy of Control[3]



2 The National Institute for Occupational Safety and Health (NIOSH)
3 *ibid*



Sample System Design

What are the criteria we should consider when thinking about sample system design?

- ## Simplicity

  The sampling process should be made as simple as possible so that the room for error is greatly reduced or eliminated entirely. This means that there should be as few procedural steps as possible to grab a sample.

- ## Ergonomics

  The system should be designed in such a way that a sample can be extracted safely without unnecessary difficulty (eg. having to reach around a face shield with a bottle to grab a sample). Using the system should be as intuitive as possible so as to minimize the risk of error.

> IN THE CONTEXT OF INHERENTLY SAFER, SIMPIFLY MEANS DESIGNING THE PROCESS TO ELIMINATE UNNECESSARY COMPLEXITY, THEREBY REDUCING THE OPPORTUNITIES FOR ERROR AND MISOPERATION
>
> **- D.C Hendershot, 2012**

- ## Minimize exposure

  Having to flush and purge into a receptacle before taking a sample exposes employees to unnecessary exposure risk. If the product cannot be recycled, it must be neutralized or disposed of. This generates waste and can represent a significant cost to the company. An inline solution will not only get rid of this process, meaning less risk of exposure and less cost, but also guarantee a representative sample everytime. If the new system is engineered to a high enough standard that ensures no dead space, it would ensure no product is left to influence the next sample.

- ## Robust design

  The sample system should have a robust design to withstand the rigours of weather conditions and constant reuse. Small tubing and quick connects are not robust enough to handle continuous use and present potential leak points which must be replaced frequently.

- ## Easily maintained

  Designing a system which is easily maintained is a key factor in sample system design. Ideally, a sample system should be relatively easy to maintain, and spare parts easily sourced, so that a regular Preventative Maintenance schedule can be carried out to ensure system integrity. Systems that are difficult to maintain run the risk of equipment failure and quickly fall into disrepair so that they are either bypassed or a cruder system is designed in its place.

- ## Minimize Emissions

  There must be no release of sulfuric acid into the atmosphere. Where possible, valves which feature Certified Low Leak Technology should be installed.

Examples of Sample Systems Currently in Use

Sample systems for sulfuric acid vary widely throughout the chemical industry.

Many plants have opted for homemade systems which consist of a double block and bleed system using ball valves. There are several flaws inherent in these systems which impact directly on safety, industrial hygiene and sample quality. Before a representative sample can be taken, a length of piping or tubing must be flushed by the Operator.

This not only increases the amount of sulfuric acid handled by the operator but it increases the complexity of the process, the exposure risk, as well as the amount of steps required to take the sample.

Additionally, if the process is not done correctly, the sample may also be compromised, which leads to poor quality samples. In an alkylation unit within a refinery where acid strength must be closely monitored, skewed results can have catastrophic consequences for both safety and the bottom line.

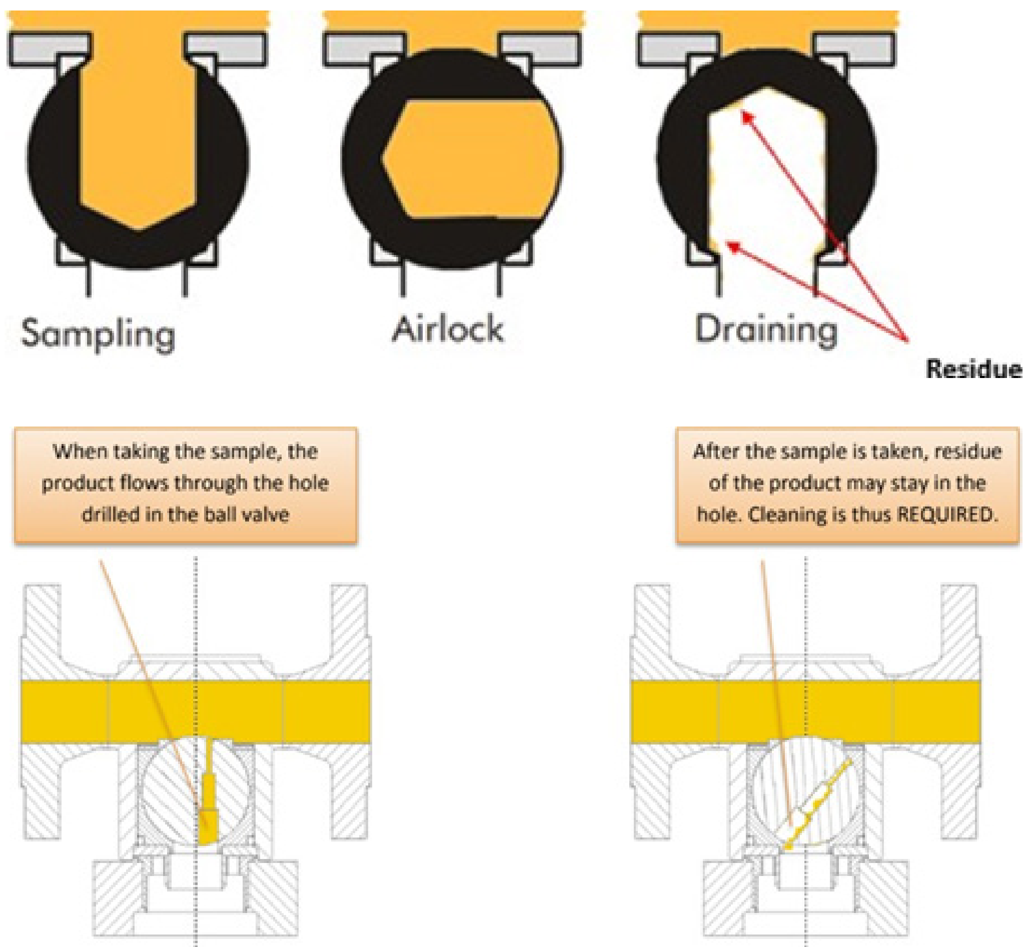
Let's look at a few examples.

▲ A loose section of tubing connection from a sulfuric acid sample station responsible for the release of 84,000 pounds of sulfuric acid into the environment.[4]

▲ The picture is a home made system and consists of a pipe from the process line to a sulfuric acid sample box. The pipe from the valve (top right) to the sample box (bottom left) must be purged before a representative sample can be taken. This not only produces waste, but if not flushed correctly leftover residue may influence the next sample.

4 CSB, Page 16

Some plants have opted for ball valve type inline sample systems for hazardous chemicals. While these are, in many cases, a better option in terms of safety compared to home made systems, they present their own issues relating to their individual designs. If we look at two types of inline ball valves commonly used for sampling hazardous liquids, we can clearly see the design flaws that render these types of valves unsuitable for sampling hazardous liquids.



Even if these systems are installed on a process line, they present Industrial Hygiene and sample quality issues. They must either be cleaned out or flushed out before the Operator can be confident that a representative sample can be collected.

Meeting the Challenge: Sampling Sulfuric Acid

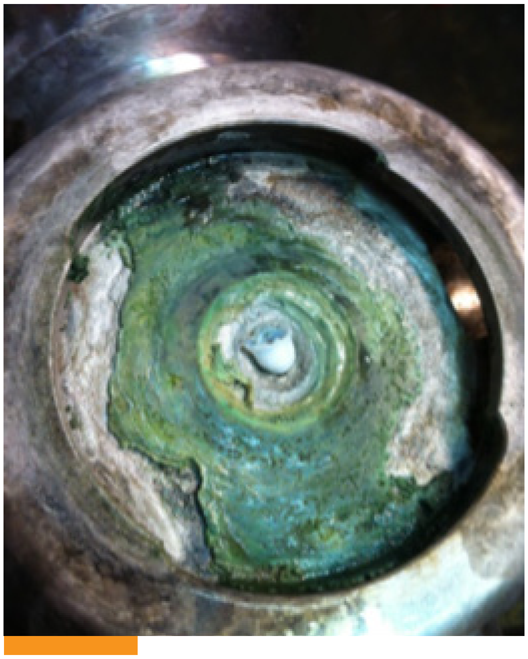
The particular characteristics of fuming acids such as sulfuric acid pose challenges which must be taken into consideration when considering sample system design.

- **Material of Construction**

  Sulfuric acid in certain strengths and temperatures will react with stainless steel and cause excessive corrosion. If sulfuric acid comes in contact with the atmosphere, sulfate can form and will plug small diameters. As PFA is resistant to sulfuric acid corrosion it is an excellent substitute for the more expensive alloys that offer corrosion resistance to sulfuric acid. A PFA lined sample system is therefore a better option for high corrosion applications.

  When considering a system for sampling sulfuric acid, acid strength and temperature will determine the materials of construction most suitable for the process.

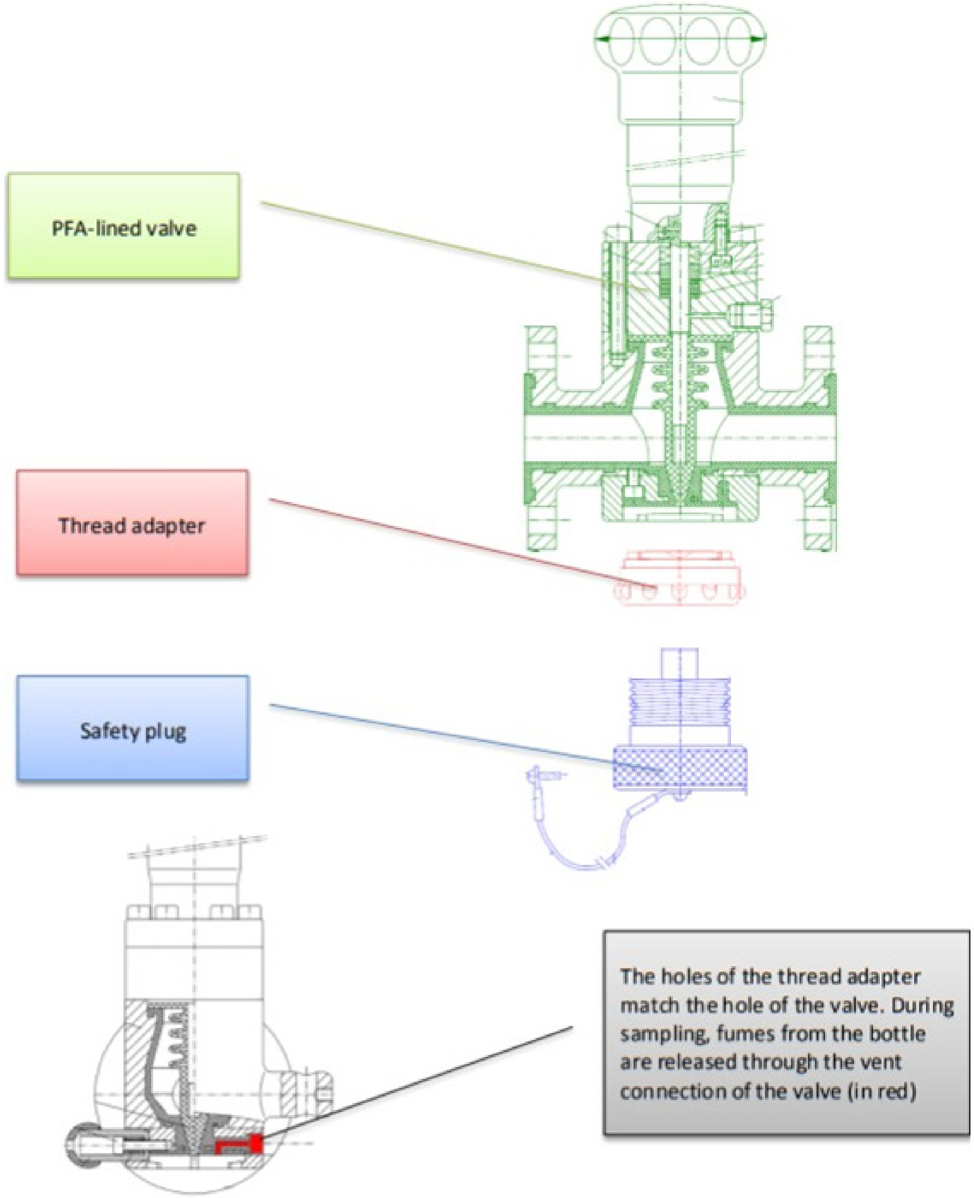
▲ Sulfuric acid corrosion on a stainless steel valve spindle



▲ Stainless steel valve outlet with sulfuric acid exposure

- ## Minimize Exposure

  An engineered solution to reducing exposure risk is the most effective way to prevent sulfuric acid burns and exposure to acid mist. Sulfuric acid will react with moisture in the atmosphere and produce a highly visible acid mist which can lead to severe irritation of the eyes and respiratory tract in high concentrations. While collecting the sample, the operator must be protected from acid fumes at all times. Sampling systems which feature numerous connections and tubing are potential sources of leaks, particularly if they are not robust.



The diagram above shows a typical BIAR PFA-lined sample valve used for sampling sulfuric acid into a bottle. As it can be installed directly on the process line or a bypass /fast loop, the sample is directly representative and no flushing or purging is required. With this system the bottle is screwed directly onto the valve using the thread adapter. There is a vent connection on the valve which corresponds with the vent on the thread adapter which allows the air inside the bottle to escape so there is no build up of pressure in the bottle. These fumes can be vented away from the Operator by way of a vent line to a scrubber. When the sample has been taken, the safety plug can be screwed back onto the valve.

Summary

The process of Sampling hazardous chemicals like sulfuric acid can be made safer with the '**effective implementation of inherently safer design and the hierarchy of controls**'.[5]

We have identified some of the risks associated with different types of sample systems and discussed a design that could potentially reduce the incidents of accidental exposure and releases into the environment. An engineered solution specifically designed to reduce emissions, waste and exposure risk which offers simplicity and reliability must be considered an inherently safer design.

Additionally, having an accurate representation of the process leads to better efficiency, less waste and less cost in the long run. Sample systems designed with piping or tubing which must be flushed before a representative sample can be taken introduces complexity to the process, and may lead to inaccurate samples. Whenever hazardous chemical sampling is a requirement, and a safer alternative is unfeasible, adequate engineering controls should always be considered as a safer alternative.

Personal Protective Equipment (PPE) should always be the last line of defence.

5 CSB, Page 17.

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Customers

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About Us

BIAR Sampling Systems was established in the early 80’s by Guy Masson, a chemical engineer working with hazardous chemicals in Switzerland.

Tasked with finding a solution to safely sample hazardous chemicals, Guy invented the PRISEMASSON® sampling system which became the first sample system to feature a hand Wheel and conical seat. Now, with over 40 years of experience, we continue to pioneer innovations in the field of chemical sampling and produce a range of valve configurations with unmatched

quality and precision. There is simply no shortcut when the health and safety of operators and the surrounding environment are at stake.

All our valves are fitted with a spring-to-close system to prevent any spillage should the operator suddenly step away from the valve. This may be in the form of a hand-wheel, lever, or pneumatic actuator, depending on the nature of the system. For example, for viscous liquids that are not under extreme pressure, the spring-to-close lever actuator will provide a better solution than our standard spring-to-close hand-wheel. By taking the time to thoroughly characterize the specific details of a customers’ application, we can provide them with the optimal sampling system tailored for their sampling needs.

Our valves are used in a myriad of challenging applications; liquids that pose thermal or toxic hazards, applications that demand an aseptic sampling environment or are atmosphere sensitive, to extremely toxic

liquefied gases such as phosgene and chlorine. To meet such a wide ranging array of needs, we have established a strong global network

that consists of a knowledgeable sales staff and distributors who work to customize each sampling valve to meet the customer’s application. Aspects such as the chemical in question as well as the temperature,

pressure, and pipe size of the given process system must be established in order to specify the correct valve type and its receptacle.

For more information please visit: **www.biar.us**

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