Valves for Sour Services

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Valves for sour services – a short refresher

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It started with crudes – as does everything in this business.

- The first commercial oilfields, in Pennsylvania, happened to contain light, sweet crude.
  - Primary products in the 1860s-70s were lamp oil and kerosene, which needed minimal refining, and paraffin for candles
  - The first heavy constituent to be ‘refined’ was petroleum jelly, refined from a waste product called ‘rod wax’
  - Developed by Robert Chesebrough, whose company was acquired by Standard Oil in 1881 and became independent again after the trust breakup of 1911
In the 19th century oil fields, crude oil was stored like water, in open tanks.

Pressure from the wells was dissipated to atmosphere.

Gases were flared, slops were run off into ditches.

Fields discovered later were not so sweet, and H₂S started to turn up in fields all over the world.

- The term ‘sweet’ comes from water. ‘Sweet’ water was drinkable, with not too much alkali or salt.
In the early days of the oil industry, uncontrolled releases of H2S and other constituents killed and injured many oilfield workers, bystanders, and even farm families who happened to be downstream.

At first poorly understood, the substance generically called ‘poison gas’ has a distinctive rotten egg smell in low doses.

A release with a high enough concentration to kill often causes a first symptom of deadening the sense of smell, causing the victims to not realize the need to escape.
H₂S characteristics

- The odor of H₂S is detectable at < 10 ppm concentration
- Eye irritation occurs at 10 – 20 ppm
- Olfactory nerve paralysis occurs at 150 – 250 ppm
  - This is the mechanism causing the victim to no longer sense the danger
- Pulmonary edema at 300 – 500 ppm
- Lethal in 50% of humans at 800 ppm for 5 min
- Immediately fatal at 1000 ppm (0.1% concentration)
While H$_2$S was present in many crude streams, it was also present in natural gas production.

Concentrations of H$_2$S in crudes of that era were often at ppm levels, but in gas deposits it could be up to several percent

- Also called ‘acid gas’ since water present in the gas led to sulfuric acid concentration.

The Claus process (first patented 1883) became the primary method for treating H$_2$S

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\begin{align*}
2\text{H}_2\text{S} + 3\text{O}_2 & \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O} \\
2\text{H}_2\text{S} + \text{SO}_2 & \rightarrow 3\text{S} + 2\text{H}_2\text{O}
\end{align*}
\]
History of corrosion

We deal with lots of corrosive fluids. What’s so special about this one?
It’s because the effects of H₂S on susceptible metals often take the form of cracking (SCC or sulfide corrosion cracking), which leads to sudden and complete (catastrophic) failure.

- You can’t catch cracking in progress, the way you can catch metal-removal corrosion by monitoring thicknesses.

Uniform and non-uniform thinning of pipe walls due to metal-removal corrosion was controlled by the development of corrosion allowances and tools for examining thickness.

- First sentinel drilling, eventually ultrasonic thickness measurement
But the presence of H$_2$S caused cracking and sudden failure alongside and in addition to metal removal.

H$_2$S reactions liberate hydrogen, which permeates steel, seeks out voids, pressurizes and expands, causing the cracking.

National Association of Corrosion Engineers was the first organization dedicated specifically to corrosion in process equipment.
- Now called NACE International, headquartered in Houston area

Founded 1943 by eleven pipeline engineers

Original focus was cathodic protection of pipelines from external corrosion, based on work begun in the 1930s
The 50s and 60s began the era of research into equipment damage caused by sulfur compounds in hydrocarbon processing.

McConomy, beginning in 1961
- Sulfur compounds only, not involving the additional presence of hydrogen in the process stream

Couper and Gorman, beginning in 1963
- Elevated temperature H₂S and hydrogen

NACE led the research, with publications like
- RP0472, Methods and Controls to Prevent In-Service Cracking Carbon Steel Weldments in Corrosive Petroleum Refining Environments
The result was NACE MR-01-75, the first MR (Material Requirement) published that year.

There was a new issue of MR-01-75 every one or two years, as research progressed on other materials important to sour services
- Designation later modified to MR0175-(year)

Supported by service experience or test data from NACE (Test Method) TM0177

While some users continued to maintain their own definition of sour service, most adopted the MR0175 limits.
The most important part of MR0175 was its limits on where SCC was known to occur, essentially a definition of sour service.

The original standard had curves for H2S partial pressures in gas, and in sour multiphase systems,

Above those curves, the service was considered sour and subject to stress corrosion cracking, and qualified materials were required. This was the region of the ‘NACE valve’.

Below those limits the service was not considered sour, and standard materials were acceptable.
History of corrosion standards

- A fatal accident in 1975, about the time MR0175 was first released, demonstrated the significance of this problem,
- And demonstrated how much more was still unknown.

- During the same period, the EFC (European Federation for Corrosion) issued similar documents,
- Leading to ISO TC 67 forming a working group to prepare a document from the EFC and NACE publications.
ISO 15156 was first published in 2002, as the first co-branded document succeeding MR0175.
- Part 1 for general information
- Part 2 for steels and low alloys
- Part 3 for high alloys

The same general information is presented as in MR0175 from its beginning, just in an expanded format with more detail

There is more emphasis on the owner supplying information about the fluid composition.
The scope of the NACE (later ISO) document was expanding to cover chloride stress corrosion cracking and other conditions endemic in upstream and production services.

Downstream and refining applications had relied on MR0175, but by 1997 it was apparent that a separate document covering problems specific to refining was needed.

A new task group was formed in 2000 to create a document specifically covering downstream processing.
The result was MR0103, first issued in 2003.

While based on the MR0175, the criteria for determining what is ‘sour’ are different, and some common upstream conditions that are rare in refining were dropped.

More coverage of sour water and the presence of ammonia and cyanides

There is more coverage of materials not used upstream, and more coverage of welding requirements not commonly found upstream.

Many paragraphs are identical to MR0175.
MR0103 has gone through several editions, has been accepted as an ANSI standard and then also adopted as an ISO standard.

ANSI/NACE MR0103 / ISO 17945 was first issued in 2015.

The successor document to MR0175, now ANSI/NACE MR0175 / ISO 15156, was also revised in 2015. As before, it is now solely focused on oil and gas production equipment.
The most important part of MR0103 is its limits on where SCC is known to occur, essentially a definition of sour service.

A system containing free water and either –
- A minimum total sulfide content, or
- A much smaller sulfide content with low pH, or
- A much smaller sulfide content with high pH and dissolved cyanide, or
- A small partial pressure of gaseous H2S with a system also containing free water.

Above those limits, the service is considered subject to stress corrosion cracking.

Subtly different from MR0175 approach, but broadly similar.
Additional emphasis is placed on temperature excursions, where materials permeated with hydrogen at elevated temps could be subject to cracking when brought to ambient.

Material selections, and specific conditions, are both spelled out for a variety of common process materials of construction.

<table>
<thead>
<tr>
<th>Material group or application</th>
<th>Conditions allowed</th>
<th>Applicable material requirement clause(s)</th>
<th>Applicable fabrication requirement clause(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steels</td>
<td>a) Hot-rolled; b) Annealed; c) Normalized; d) Normalized and tempered</td>
<td>13.1</td>
<td>13.1.7, 13.1.9, Clause 15</td>
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How to specify a valve for sour service

Now for some practical advice.....
The following terms are often thrown around –

- Sour service
- Wet sour service
- Wet H₂S service
- Aqueous H₂S service
- SCC service (stress corrosion cracking)
- SSCC service (sulfide stress corrosion cracking)
- SSC service (sulfide stress cracking)

Although there are real differences between some of these terms, in practice many engineers take them to mean about the same thing.
Specifying valves for sour service

- It’s important to define the term(s) you use in your purchase specifications.
- It’s important to understand exactly which corrosion problems you do or don’t have.
- You still need to describe the details of the materials you need in the valves.
- It’s really not a good idea to just say you want a NACE valve.
Which standard(s) apply?
- MR0175/ISO 15156 or MR0103/ISO 17945?
- One consequence of this choice is that the owner needs to supply much more information for MR0175
  - Fairly easy if you know the current and future composition of the field
  - Water injection can make produced oil sour when first production was not

What’s your default valve choice?
- Gate, ball or other? Based on API standards?
- Made by manufacturers who know what this means?
API standards 600, 602, 608 and 623 now include MR0103 as an option, mostly in ‘Information to be supplied by Purchaser’.

API 6D references both MR0103 and MR0175, useful since there are still a lot of callouts for this standard in downstream.

You can make almost any steel valve suitable for wet sour service, if you start at the beginning.

You probably can’t convert one that is not already suitable.
You always need to know enough about the service to tell whether it qualifies for the definitions of sour service.

You need to know what other corrodents are present that might mitigate or complicate the effects of sulfide corrosion.

You also need to have an idea whether these are normal, or occasional, or upset conditions.

We’ll confine this discussion to services covered by MR0103.
The standard begins by emphasizing the action of water and H₂S on materials under tensile stress, producing corrosion and cracking.

Sulfide corrosion produces hydrogen, hydrogen causes cracking.

Parameters at work in SSC include –
- Chemical composition. Strength (hardness), Microstructure (killed steel)
  - Total tensile stress (in piping, you can improve this by PWHT)
- Hydrogen flux (a function of chemistry and pH)
- Temperature and time
The data you need is similar to the ‘old ways’ of MR0175

It’s not an exaggeration to say that the original MR0175 ‘grew up and went its own way’ to focus on upstream needs and practices, while the refining business needed something less complicated and more specific

– The stream complexity in refining is complicated enough
The emphasis in materials selection is on susceptibility to SSC

- Materials somewhat susceptible under lab test may perform OK in service
- Materials with low susceptibility overall may have high susceptibility under certain conditions (shutdowns, for example)
  - Improper or inadequate heat treatment
  - Weld metal deposits
  - Heat affected zones
  - Other residual stresses
Specifying valves for sour service

- If it’s below the limits in the standard, a service is not considered sour and normal piping materials can be used
  - No special hardness control, no special limits on material, anything you use in normal hydrocarbon service is OK
- There must be free water in the system for the service to be wet sour!
  - Look at lines with operating temp above about 300 F, apply insulation or tracing, be sure they’re free-draining
- There is no curve per se, unlike the early MR0175, but a set of limits on SSC parameters
  - ppm H\textsubscript{2}S with water, or low pH and H\textsubscript{2}S, or high pH and H\textsubscript{2}S with cyanides.
Differences between downstream and upstream in terms of service

- Chlorides (water) tend to be present in lower quantities in process lines
- Still not absent, still have to avoid 300 series stainless in certain locations
- CO\textsubscript{2} tends to be present in much lower quantities than upstream
  - Therefore the buffering effect on pH does not occur
- Effects of temperature
  - Increase the charging rate of hydrogen
  - Systems can absorb hydrogen at temperature, crack at ambient
- Effects of pH
  - Higher or lower than neutral pH increases hydrogen flux
Fluids in sour service are still fluids,
- You’ll still need all the valve varieties you’d need anywhere else
- block, check, throttling, control, vent and drain, ...

Early adopters of sour service specs in refinery service tended to go with alloy 400 trim (API 9 or 11)

The most common choice now is 316 trim (API 10, 12 or 16)

Each has drawbacks
- Alloy 400 (Monel) trim materials are not very strong
- 316 trim has chloride problems
Specifying valves

- Trim 5 or 8 is perfectly good for services that are not especially corrosive other than for the H₂S
- Trims 5, 8, 11 and 12 may have exactly the same body seat construction and material
- There is some use of alloy 600 or 625
  - No trim numbers yet
  - These alloys are immune to chloride cracking
  - Material examples: A494-CW6MC castings, B443 plate, sheet and strip, B446 bars and rods, B564 forgings, B637 for springs and stems
As with all other cases of SSC, hardness control in valves is very important.

Natural hardness of finished ASTM A105N or cast carbon grades should be adequate:
- Hardness control not that difficult to achieve.

Many high alloy components need very specific heat treat conditions:
- For example, 17-4PH H1150 double heat treated.

Welds in valves can be significant:
- Sealwelds attaching seat rings to body, or at bonnet.
- ‘Cosmetic’ weld repairs.

And there is no 1% max limit on nickel in carbon steels.
Hardness measurements are easiest to verify compliance

High alloys make reference to their PREN
  - Pitting is not addressed, this is only a mechanism to categorize alloys known to also resist cracking

Hardfacing alloys
  - OK when base material meets hardness requirement after overlay welding

Bolting
  - Use specifically permitted grades with lower hardness, if exposed to H₂S
  - No limitation if non-exposed (not exposed to sour environment)
  - No zinc or cadmium plating, because they enhance hydrogen generation
Specifying valves

Examples:

Item Code: 5156169
Abbreviated Description: GATE 150# RF STL, 316/STEL GO H2S
Purchase Description:

ITEM - GATE VALVE, OS&Y-BB
RATING - ASME CLASS 150 FLANGED, RAISED FACE
OPERATOR - ENCLOSED BEVEL GEAR OPERATOR
MATERIAL
  BODY & BONNET - CARBON STEEL
  CASTINGS - ASTM-A216, GRADE WCB OR
  FORGINGS - ASTM-A105
  TRIM - 316 SS WITH STELLITED SEATS
  BOLTING - ASTM-A193 GR B7M W/ GR 2HM NUTS
SERVICE - FOR WET SOUR SERVICE - NACE
STANDARDS - API 600 / ISO 10434
Thank you very much for your time