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SUBJECT: In-Pile Loop Valve Problem

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ORNL
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On February 27, 1956, the In-Pile Loop operations group transferred three valves from the sampling system of the HB-4 installation to this group for examination. These were the standard Autoclave Engineering high pressure valves with type 304 stainless steel bodies and type 420 stainless steel stems. Valve No. 2 was plugged between the high pressure and low pressure ports. Valve No. 7 was leaking between the high and low pressure ports. Valve No. 15, a three way valve, was clear between the two high pressure ports but was plugged between the high pressure ports and the low pressure port. We were asked to determine the location and if possible the cause of the valve failure in each case.

The valves were washed with water to remove any external contamination and since the remaining activity level was quite low the remainder of the examination and dismantling was done directly.

Figure 1 is an exploded cut-away view of the valve construction and will be used in discussing the observation on the various valves. The various ports on the valves were carefully examined before disassembly. After this examination the valve stems were turned to see if they were operable. Finally the bronze nut was unscrewed and the stem assembly removed for examination and photographing. Some samples were taken for both metallographic and chemical analysis.

For purposes of clarity each valve will be reported separately.

Valve No. 2-- The low pressure port on this valve was covered with a rust colored scale while the high pressure port was apparently free from any such deposits. On removal of the stem assembly the region around the valve seat showed a large accumulation of similar rust colored material. This crud was collected for chemical analysis. The valve stem itself in the region of the tapered end appeared to be heavily corroded and damaged. Figure 2 is a photograph of this valve after disassembly. The scale deposit at the low pressure port and the heavy

damage to the stem is apparent. The extreme tip of the tapered section of the stem was found in the valve seat. The surface of this tip exposed to the high pressure region was bright and shiny. Two samples of this valve stem were sent to the Hot Metallography group, the damaged end and a portion from the handle end which had not been exposed to solution. Additional samples were sent to Analytical Chemistry for analysis and to J. L. English for laboratory corrosion tests. Mr. English will report his findings separately. The results of the chemical analysis of the stem material together with the analysis and heat treatment supplied by the manufacturer are listed in Table I. With the exception of the sulphur and the selenium, which was not reported by the manufacturer, the analyses agree and are well within the specifications for type 420 stainless steel. The chemical analysis of the crud removed from the valve is listed in Table II.

Valve No. 7-- Examination of both the high and low pressure ports on this valve showed them to be free from any accumulations. On disassembly the valve stem was found to be broken between the stainless steel spacer and the stainless steel packing washer. The area of this fracture is shown in Figure 3. Figure 4 is a photograph of the remainder of the stem after removal from the valve body. It is quite evident that this region has failed by brittle fracture. There was no accumulation of material on any of the surfaces of this valve.

Valve No. 15-- Valve No. 15 differed from the other two valves in that it was a three way valve. As shown in Figure 1 the two high pressure ports are continuously connected. Examination of the two high pressure ports showed them to be free from any accumulations. The low pressure port on the other hand appeared to be completely plugged with a rust like scale. On disassembly the area of the valve seat contained a considerable quantity of rust colored material. The chemical analysis for the material from the low pressure port and the seat area is listed in Table II. It is of interest to note that some of this material was

apparently metallic.

Figure 5 is a photograph of Valve 15 after disassembly. As with Valve No. 7 the stem had been broken between the stainless steel packing and spacing washers. The tip of this stem was found still in place in the seat area. However, the stem immediately behind this tip appeared to be badly corroded. The corroded portion of the stem was also sent to the Solid States Division for metallographic examination.

Discussion of Findings

The results of the metallographic examination have been reported previously⁽¹⁾ and only a portion of these results will be included here for purposes of discussion.

In the case of Valve No. 7 it is the author's opinion that the failure was purely mechanical. The fracture surfaces indicate a brittle break such as might be expected from this hardened stem and there is no indication on any of the surfaces of any corrosion attack. It would appear that the conical portion of the stem cracked under loading and that subsequent efforts to operate the valve resulted in the stem fracture shown in Figure 3.

The failure of Valves No. 2 and No. 15 are a different matter. Certainly they show signs of mechanical damage such as the fractured stem shown in Figure 5. However, the rough rust colored surfaces of the tips of both these valve stems, the metallic cores on the particles removed from valve No. 15 seat area and the metallographic findings indicate that the original cause of failure was corrosion of the valve-stem material. The type of corrosive attack can be seen in the metallographic pictures. Figure 6 is a typical section through the valve stem in the unaffected handle region. Figures 7, 8 and 9 are typical sections through the valve stems in the region of the failures. The attack is localized in the grain boundaries and the depth of attack is reported to increase

as one approaches the area of actual failure.

The presence of uranium in the rust-like accumulations indicates that the solution trapped in the valve between the seat and the low pressure port may have been reduced and thus contributed to the rate of corrosion attack.

The difference between the high and low pressure surfaces of the tips on the valve stems from Nos. 2 and 15 is difficult to reconcile. One possible explanation may be the stress imposed on the portions of the stem in the low pressure region when the valve is closed.

A recent report⁽²⁾ discusses the stress-corrosion cracking of Type 420 stainless steel in 90 psi saturated steam. In this case, the author demonstrated the effect of residual surface stress in causing stress corrosion cracking even with "stress-relieved" material. Here the residual stress or the applied stress from closing the valve may have influenced the corrosion of these stems.

Whether the failures here reported are instances of stress corrosion cracking or of grain boundary corrosion of a sensitized steel cannot be defined. Certainly the wide variations in grain size and stem hardness leads one to wonder about the manufacturer's quality controls.

Recommendations

At the insistence of Mr. D. T. Jones, the author undertook a rather extensive literature search in an effort to find some possible leads as to the cause of failure and suggestions that might reduce their future probability. Unfortunately the amount of information on Martensitic stainless steels under corrosive conditions similar to ours is very limited. Perhaps the most informative reference is Monypenny's "Stainless Iron and Steel"⁽⁴⁾. He covers the entire field of effects but of particular interest are his findings on the effects of small additions of copper sulphate in dilute sulfuric acid solutions. In concentrations near those we encounter, he reports reduction of the copper

and higher corrosion rates on the martensitic stainless steels. Unfortunately, the nature of the corrosion attack is not detailed although in general he reports increased attack of these steels results in pitting. It is the opinion of Professor Hackerman, who was consulted on this problem, that the attack might change from general to pitting or to intergranular in nature with only very minor changes in exposure conditions or corroding media. Only one reference to intergranular failure was found. M. A. Schiel⁽⁶⁾ reported such a failure in a stressed, fully-hardened, Type 421 stainless steel specimen exposed to boiling $MgCl_2$ solution.

For convenience, the various recommendations will be listed with reasons for their suggestion.

(A) Chemical Composition

(1) High Chromium Content. It is well known that increasing chromium content increases the passivity of the various stainless steels. In general, a minimum content of 12% effective chromium is needed. Since precipitation of 0.1% of carbon as chromium carbide will remove approximately 1% of chromium from solution and render it ineffective, it is particularly important to keep the chromium high in a high carbon alloy such as this.

(2) Minimum Carbon Content. This, of course, must be determined by the physical characteristics required, particularly hardness. However, because of its effect on the chromium, the smallest amount necessary is advisable.

(3) Sulphur and Selenium Combined. This should be held to less than 0.02% as specified. They are known to reduce the corrosion resistance in general and specifically they may promote failure by corrosion fatigue by their presence as non-metallic inclusions, affording both notch effect and the generally undesirable presence of a second phase⁽³⁾.

(4) Other Impurities. The specifications as written for Type 420 would appear to be quite adequate.

Note: It has been suggested by the heat treater that a foreign element, perhaps lead, was contained in the bad heat. At this time, the writer has no proof of such an element. One microstructure does show a precipitate localized in the grain boundary. Certainly any tramp elements which would precipitate in these regions could enhance the possibility of intergranular attack.

(B) Heat Treatment

Without specifying a heat treatment cycle and in view of the recent information concerning the current heat treating techniques, one recommendation seems necessary. Several authors have clearly shown that tempering above 750°F, particularly as high as 1000°F, definitely has an adverse effect on corrosion^(3,4,5). I would like to quote W. O. Binder⁽⁵⁾, who describes it very concisely. "The martensitic steels must be properly heat treated to exhibit good corrosion resistance, and although they normally show maximum resistance to corrosion in the fully hardened condition, relief of quenching stresses coupled with greatly improved ductility and toughness may be obtained by tempering these steel at temperatures up to 400 degrees Cent. (750 degrees Fahr.) without seriously reducing their corrosion resistance. Tempering between 400 and 600 degrees Cent. (750 and 1110 degrees Fahr.), however, should be avoided, particularly when the carbon content is high, as this range of temperature imparts low toughness as well as low corrosion resistance."

Certainly the failure of Valve No. 7 indicated a lack of ductility. Also the wide range of grain size, and the amount of precipitated carbides in the microstructure indicates an uneven and perhaps too high an austenitizing and/or tempering temperature. The austenitizing temperature should be held to 1850°F to reduce grain growth and the tempering temperature should be less than 750°F.

(C) Machining Techniques

These seem to be well within the recommended procedures with finish

grinding removing the surface layers containing high residual stresses.

References

- (1) W. B. Parsley, et al., "Metallographic Examination of HRP In-Pile Loop Valves V-2, V-15 - - - - -", ORNL-CP-56-7-2 (July 3, 1956).
- (2) G. Klingel, "Stress-Corrosion Cracking of Stainless Steel", Metal Progress, Vol. 69, No. 4, pp. 77 and 78 (April, 1956).
- (3) C. A. Zapffe, "Stainless Steels", American Society for Metals, Cleveland, Ohio, pp. 66-68 (1949).
- (4) J. H. G. Monypenny, "Stainless Iron and Steel", John Wiley and Sons, Inc., New York, Third Edition (1951).
- (5) W. O. Binder, "Corrosion of Metals", American Society for Metals, Cleveland, Ohio, p. 58 (1946).
- (6) M. A. Scheil, "Some Observations of Stress-Corrosion Cracking in Austenitic Stainless Alloys", ASTM and AIME, p. 406 (1944).

Table I

Chemical Analysis and Heat Treatment of Valve Stems

	<u>Manufacturer</u>	<u>ORNL</u>
C	0.36%	0.31%
Mn	0.47	0.43
Si	0.27	0.32
S	0.007	0.0155
P	0.025	0.02
Cr	13.72	13.42
Ni	---	0.196
Se	---	0.012

Manufacturer: Universal Cyclops; their designation: Uniloy 1435 (type 420); heat number: H-3500.

These stems were hardened in a disassociated ammonia atmosphere furnace with the following heat cycles:

Stems enter furnace at 1400°F, temperature raised to 1600°F in five minutes.

Temperature increased from 1600°F to 2000°F in ten minutes, of which time pieces were at 2000°F for approximately three minutes.

Temperature lowered to less than 1000°F in chilled section of furnace. Furnace cooled from here in 1-1/2 hours.

This heat treatment should give a R_c hardness of 48 to 50.

Table II
Chemical Analysis of Crud Removed from Valves

	Valve 2 Low Pressure Port	Valve Stem	Valve 15 Low Pressure Port	Stem and Seat Region
Weight	5.65 mg	4.05 mg*	13.5 mg	5.41 mg**
U	6.35%	0.29%	11.11%	16.64%
SO ₄	0	0	0	0
Cu	1.72%	2.74%	2.91	1.18
Cr	10.48%	2.99	12.10	0
Ni	0.35%	6.42	0.22	1.18
Fe	35.40	0.37	30.37	29.57
Ti	0	0	0	0
Al	0	0	0	0
Mn	-	-	-	0
Zr	-	-	-	0.46

* Valve 2 - Valve stem crud contained some small particles which were insoluble in HNO₃, HCl or HF solutions. These are thought to be part of the Teflon packing gland.

** Valve 15 - Stem and seat region crud originally weighed 71.45 mg. Treatment with HCl solution dissolved the rust-like scale leaving a residue of bright metallic particles. These were probably portions of the stainless steel stem. Reweighing these particles provided the 5.41 mg weight difference for percentage calculations.

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FIGURE 1
CUT AWAY VIEW OF HIGH PRESSURE AUTOCLAVE ENGINEERING VALVES

Fig. 2 Valve No. 2 After Disassembly

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Fig. 3 Valve No. 7 After Disassembly

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Fig. 4 Remainder of Valve No. 7 Stem Assembly

Fig. 5 Valve No. 15 After Disassembly

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RMG 1404

250X

Figure 6 Longitudinal Section Through Valve Stem in Area of Handle.

RMG 1405

250X

Figure 7 Typical Corrosive Attack of Valve Stems From Valves No. 2 and 15.

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RMG 1406

250X

Figure 8 Typical Failure Area of Valve Stems From Valves No. 2 and 15.

RMG-1407

250X

Figure 9 Failure Area of Valve Stem from Valve No. 2 Showing Some Mechanical Distortion.

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