valves in the original pumps[7] were mushroom type, with large-radius valve face and conical seats of AISI Type 440-C stainless steel. These were eroded after a few hours of service.

Balls 2 in. diam of the same material hardened to Rockwell C-56 on conical stellited seats gave 2 weeks of service. With this type valve, line contact is achieved, and hard particles are either cut or washed from the surface. Cracks have developed occasionally at the terminal junction of the welded stellite seats causing erosion. In others, the stellite has deformed to the shape of the ball, offering wider contact surface for particle build-up initiating erosion, Fig. 18.

Other materials tested include a 12 per cent chrome ball valve with graphitic tungsten tool-steel valve seats hardened to 52 RC. After approximately 360 hours of service on water and clean oil, the graphitic-steel seat was eroded very deeply in one narrow zone. In the same service an alternate chromium-vanadium steel seat was eroded lightly at many points. Spring-loaded, mushroom-type, high-chrome valves with a 45-deg conical face and seat have proved more satisfactory in clean-liquid service.

Cast uniform-hardness ring-type stellite inserts with $^3/_{32}$-in. contact surface have been prepared for the next liquid-phase run for paste service.

Other Metal Failures

Fatigue of Pump Blocks. The high-pressure injection pumps, as originally designed, had many sharp edges at the intersection of the valve ports with the main cylinder bore.[7] There were also sharp edges where transverse holes intersected the plunger bore. These transverse holes were closed with threaded and seal-welded plugs. After relatively short service, the seal welds cracked and could not be repaired satisfactorily.

After 300,000 stress cycles, cracks also developed at the narrow section between the discharge and inlet-valve ports. New blocks with smooth internal surface finish, a minimum of openings, and fillet radii of $^1/_8$ in. minimum have operated without failure for over 3,000,000 cycles.

Fatigue. Steam-cylinder rods on the high-pressure injection pumps had been designed with sharp changes of section near the threads. After approximately 900,000 cycles one of these rods broke, through fatigue at the root of the thread.

Replacement rods provided with generous fillet radii at section changes have withstood several million cycles.

Some flange bolts on high-pressure vessels and pumps broke at the root of the last thread where no relief had been provided. No failures have occurred where studs have been threaded for the full length, or where there is a reduced section between the threaded ends.

Tubes Subjected to External Pressures. The high-pressure converters have a pyrometer tube 2-in. OD × $^7/_8$-in. ID of Type 347 stainless steel. This tube carries the thermocouples for measuring the temperatures at various levels in the vessels. It was designed for external pressures of 10,000 psi and temperatures up to 900 F.

During a runaway reaction in one of these units, the temperature climbed rapidly, exceeding the 1500 F limit of the recorder. It was concluded from the grain size of the metal and the very small number of cracks, that the temperature had exceeded 1800 F while subjected to the 10,000 psi external pressure. This combination of pressure and temperature caused the tube to collapse, Fig. 19.

[7] "High-Pressure Injection Pumps in the Coal-Hydrogenation Demonstration Plant," by J. T. Donovan, B. H. Leonard, Jr., and J. A. Markovits, presented at the Annual Meeting, Atlantic City, N. J., November 26–30, 1951, of The American Society of Mechanical Engineers (Paper No. 51—A-71 unpublished).

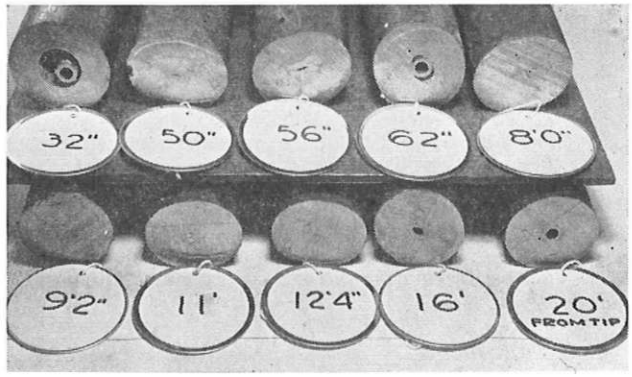

Fig. 19 Collapsed High-Pressure, High-Temperature Pyrometer Tube Showing Appearance at Different Distances From Tip

Closer temperature control through better cooling-gas distribution is expected to eliminate this hazard in future runs.

Conclusions

Although it is possible that other metallurgical problems may develop as plant operations continue, it is felt that the most serious difficulties have been discovered and solved satisfactorily. It is interesting to note that except for erosion at pressure-reduction points there was very limited metal deterioration in the high-pressure system. The corrosion in the low-pressure equipment, while appreciable, was no more than had been anticipated.

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Discussion

G. A. Nelson.[8] This paper has been read with a great deal of interest, and we wish to congratulate the authors on their ingenuity in correcting the troubles they have had with mechanical equipment operating under conditions of extremely high pressures and temperatures combined with erosive and corrosive environments. We have two specific comments to offer:

Under the heading, Hydrogen Attack, the limits for carbon and alloy steels are given and it is gratifying to find that after years of operation no trouble has been found with the piping when used under these prescribed limits. The authors show that when the limits for either carbon steel or 1 per cent chromium steels have been exceeded the effect from hydrogen is very rapid. This indicates how critically important is the proper amount of alloying elements for adequate resistance to hydrogen at high temperatures and pressures.

Under the heading, Stress Corrosion Cracking of Caustic Storage Tanks, we can confirm that the temperature limit for "as-welded" steel storage vessels handling caustic is very critical. We cite an example of a column in caustic service which had been handling dilute caustic at a temperature of about 190 F for 15 years without any trouble; however, operation of the column was found to be better when the temperature was raised to 240 F. Three months after the temperature was raised the column suffered caustic cracks adjacent to welds. It was removed from service and replaced by a stress-relieved vessel.

[8] Shell Development Company, Emeryville, Calif.

Authors' Closure

The interest which Mr. Nelson has shown in this paper is sincerely appreciated, particularly because of his familiarity with similar problems. His splendid assembly of data on hydrogen attack of carbon and alloy steels at high temperatures and pressures was referred to when the design limits for the steel in the hydrogenation demonstration plant were set. He subsequently suggested that lower alloy steels would be satisfactorily resistant for the intermediate temperature range. It was not known, however, if the mechanical properties of steels with lower chromium content would be satisfactorily stable when heat-treated to withstand the required fiber stresses. Babcock & Wilcox Tube Company has since investigated the effect of aging at 650 and 850 F on normalized and tempered Croloys $2^1/_4$, 5, and 7 (containing $2^1/_4$, 5, and 7 per cent chromium, respectively). In 5000-hr tests Croloy $2^1/_4$ was satisfactorily stable at 650 F and Croloy 7 was satisfactorily stable at 850 F. Preliminary exposure tests have confirmed the reported resistance of these steels at these same temperatures.

The case cited by Mr. Nelson of a column that developed caustic cracks adjacent to welds confirms the experience noted in the paper and further emphasizes the necessity for stress-relieving welded vessels operating at temperatures above 200 F in caustic service.