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DOCUMENT NO. HW-59752

COPY NO.

DATE March 30, 1959

ISSUING FILE

TITLE

1706 KE WATER TREATMENT FOR OUT-OF-REACTOR TEST FACILITIES.

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1706 KE WATER TREATMENT FOR OUT-OF-REACTOR TEST FACILITIES

INTRODUCTION

Water treatment systems for preparing and maintaining high purity water in out-of-reactor or in-reactor test loops are becoming increasingly important. In out-of-reactor experiments the presence of ionic impurities in the water has a marked influence on film formation and corrosion rates. It is, therefore, imperative that these impurities be maintained at the lowest practical concentration.

This report explains the water treatment methods used in the out-of-reactor loops in the 1706 KE Building. The data obtained concerning the operation of these systems has been tabulated and is included in this report.

SUMMARY

The data obtained during operation of the out-of-reactor loops indicate that both the CEP (Corrosion Equipment Prototype) feed and bleed method and the ELMO (Experimental Loop Mock-up, Out-Of-Reactor) ion exchange method of effecting loop water clean-up are satisfactory.

The make-up water pretreatment system consistently produces water with less than 0.01 parts per million dissolved solids as calcium carbonate and less than 10 parts per billion dissolved oxygen.

DISCUSSION

The out-of-reactor facilities now operating in the 1706 KE building include the ELMO and CEP facilities and the mock-up tubes. The organic loops are not considered here since no water treatment equipment is needed for these loops.

The mock-up tubes normally operate with process water so no further chemical purification is used. Small amounts of sodium dichromate and sulfuric acid are, however, added to the water to provide corrosion inhibition and pH control respectively. The mock-up tubes are equipped to operate with service water, filtered water, raw water or process water. A planned revision of the filter system now in existence and addition of a settling basin will make it possible to begin with raw river water and produce purified process water for the mock-up tubes. This system would enable the operators to determine the effects of various treatment procedures and chemical additives on the solid materials present in the water. Since the mock-up tubes do not operate with high purity water, they will not be considered further in this report. The following discussion pertains to the ELMO and CEP facilities only.

Since the operating conditions for the various experimental loops are not constant, it is necessary to have a water treatment system capable of meeting the specifications for the loop with the highest water quality requirements. Since some of the loops are operating with very high purity water, (< 0.01 parts per million dissolved solids as calcium carbonate) the water treatment system must be capable of purifying the water to a specific resistance of at least 10 million ohm-centimeters.

The required water quality for the loops operating with high purity water is obtained by ion exchange techniques. The filtered water supplied to the building is sent directly to a duplex (separate cation and anion exchangers) demineralizing system where some of the dissolved solids are removed from the water and the specific resistance is increased from about 30 thousand to > 500 thousand ohm-centimeters. At this point the predominant impurities in the water are oxygen, carbon dioxide, sodium and silica. The water then passes through a mixed bed (mixed cation and anion resins) deionizing column where the water is further purified to a specific resistance level of at least 10 million ohm-centimeters. At this point the water contains negligible amounts of dissolved solids but an appreciable amount of dissolved oxygen is still present. The water is therefore passed through a copper based deoxygenator where the oxygen is chemically removed. During the deoxygenation step copper is released from the column as cupric ion and the water is therefore passed through another small ion exchange column to complete the purification step. The water then passes into the loop make-up storage tank. The water additions to the loops requiring high purity influent water are then drawn from the make-up storage tank and added to the loops by make-up pumps. ELMO-7 is the only exception to this rule. This loop is equipped with its own make-up system. The mixed bed deionizer effluent is split before it enters the deoxygenator. Part of this stream follows the previously described path and some of it goes to the ELMO-7 make-up system. This system then effects a deoxygenation and final purification step similar to but independent of the main system.

After the deionized water has been added to the loop it comes in contact with the loop piping and test pieces and picks up some dissolved solids. This process decreases the water purity immediately. It is therefore necessary to utilize a loop clean-up system to maintain the loop water purity at the desired level. The clean-up systems for the ELMO and CEP loops are entirely different. The CEP clean-up is effected entirely by the feed and bleed method; that is, the loop bleed rate is set at such a value that there is a complete water changeover in the loop once every four hours. This eliminates the need for an ion exchange system to remove the impurities picked up in the loop. There are some difficulties encountered in this type of operation, however. It is very important that the feed and bleed rates be carefully adjusted and maintained if any reasonable pH control is to be achieved. Also for systems operating at pH conditions considerably different than the make-up water pH, frequent chemical additions or other water conditioning methods have to be provided. Since this method of effecting water clean-up does not involve special processing (water treatment) it will not be considered further. Unless specifically stated otherwise all further reference to "clean-up systems" shall refer to ELMO systems. The ELMO clean-up systems are small flow by-pass loops on the experimental loops. A small portion (about 0.5%) of the total flow is diverted through the clean-up system to maintain the required water quality. Figure 1 represents a typical ELMO clean-up system.

Operating experience has shown that the water quality can be maintained at an acceptable level by continuously purifying only a small portion of the loop water. Of course better water quality could be obtained by purifying all of the water but this would impose tremendous operating problems, e.g., cooling and reheating all of the loop water continuously. Therefore the ultimate water quality has been sacrificed slightly to make operation of the facilities much easier and more economical.

At present there are out-of-reactor loops operating at low (4.5), neutral (7.0) and high (10.0) pH with de-ionized water. The low pH systems are maintained at pH 4.5 ± 0.2 by phosphoric acid additions and use of a phosphoric acid regenerated mixed bed ion exchange resin (hydrogen-phosphate form) in the clean-up system. The neutral systems (pH 7.0 ± 0.5) are operated without chemical additions and neutrality is maintained by regulating the clean-up system flow rate through a hydrogen-hydroxyl form mixed bed ion exchange resin. The high pH systems are maintained at pH 10.0 ± 0.3 by lithium hydroxide additions and use of a lithium hydroxide regenerated mixed bed ion exchange (lithium-hydroxide form) resin in the loop clean-up system.

In general the loop clean-up systems should be designed to meet the following requirements:

1. They should help maintain the desired loop pH.
2. They should effect essentially complete clean-up of the loop water.
3. They should maintain the concentration of the exchanged ions at a constant level.

Since the clean-up systems (see Figure 1) are really nothing more than ion exchange systems, the above requirements may be established as the resin operating requirements. These requirements can impose very severe operating problems if they are not compromised with some room allowed for variation from the ideal situation.

Ultimately it is hoped that resins will be available that will be capable of fulfilling all three of these requirements simultaneously, however, such is not the case at the present time. Therefore these requirements have been compromised to obtain an operable system. The pH control is effected by ion exchange methods in the neutral systems only. In the high and low pH systems chemicals are added periodically as needed to help maintain the required loop pH. The concentration levels of the exchanged ions in the loop water are controlled by varying the amount of feed and bleed in the loop. As the clean-up system operates the concentration of the exchanged ions tends to increase. However, by controlling the amount of make-up water added to and the amount of water removed from the loop an equilibrium level is soon established. It seems obvious that some control over the magnitude of this equilibrium level can be obtained. This control is limited only by the feed and bleed flow ranges available.

Experimental programs are now underway to determine some of the physical and chemical properties of the phosphoric acid and lithium hydroxide based resins as well as their operating characteristics. However, at this time the data available are not sufficient to permit us to define the resin characteristics. The general observations thus far, however, indicate that these resins are functioning satisfactorily in the out-of-reactor facilities.

A comprehensive experimental program has been conducted to determine some of the materials present in the loop water of the various facilities as well as pH and water quality variations. The following tables indicate the experimental work done and the analytical results obtained.

TABLE I

Sample Types and Sampling Frequencies for Out-Of-Reactor Test Facilities

Loop	Sample			
	Wet Chemical	Oxygen	Gas Bomb	Hot Crud Probe
		(Samples per week)		
ELMO-5	3	5	3	3
ELMO-6	3	5	3	3
ELMO-7	3	5	3	-
Loop Make-up	3	5	-	-
CEP-1	7	-	-	-

TABLE II

Gaseous Impurity Levels In Out-Of-Reactor Test Facilities

Loop	Gas							
	CO_2	A	O_2*	N_2	CO	CH_4	He	H_2
	(Parts per million)							
Loop Make-up	0.04	0.40	0.005	20	0.04	0.01	0.004	0.005
ELMO-5	0.04	0.36	0.005	19	0.06	0.02	0.003	0.006
ELMO-6	0.06	0.72	0.010	31	0.06	0.03	0.005	0.005
ELMO-7	0.06	0.54	0.100	6	0.04	0.03	0.005	0.045
CEP-1	-	-	-	-	-	-	-	-

No data are available for CEP-1 since sample facilities have not been installed. These facilities will be installed when the loop is changed to high pH operation.

TABLE III

Metallic Impurities In Out-Of-Reactor Test Facilities

Loop	Metal								
	Fe	Ni	Cr	Cu	Al	Zr	Mn	Co	Ca
	(Parts per billion)								
ELMO-5	2	<5	<1	1	50	<1	2	<5	10
ELMO-6	40	<5	2	4	>200	<1	2	<5	15
ELMO-7	-	-	-	-	-	-	-	-	-
Loop Make-up	<1	<5	<1	1	3	<5	<1	<5	5
CEP-1	-	-	-	-	-	-	-	-	-

TABLE IV

Anionic Impurities In Out-Of-Reactor Test Facilities

Loop	Anion		
	Cl^-	$SO_4^=$	$PO_4^{\equiv}$
	(Parts per million)		
ELMO-5	< 0.1	-	0.02
ELMO-6	< 0.1	-	4.50
ELMO-7	0.1	-	0.10
Loop Make-up	< 0.1	-	0.02
CEP-1	< 0.1	<1.0	-

* The ELMO-7 oxygen data may not indicate the true free oxygen concentration since some dichromate is occasionally detected in the loop. Dichromate interferes with the oxygen analyses and indicates the presence of more oxygen than is actually present.

TABLE V

Miscellaneous Data For Out-Of-Reactor Test Facilities

Loop	Total Solids (PPM)	pH	Specific Resistance (ohm-centimeters)	Particulate Crud (PPB)
Loop Make-up	0.04	5.80	2×10^6	-
ELMO-5	10.0	9.90	8×10^4	100
ELMO-6	15.0	4.50	1×10^5	30
ELMO-7	5.0	6.60	3×10^5	-

One consistent problem has been the accurate determination of the particulate crud concentration in the ELMO-5 water. A previous test about two years ago introduced significant amounts of silica in the loop. Since that time difficulty has been experienced with crud probes plugging. The data for the particulate crud concentrations is therefore not conclusive.

The specific resistance values reported are actual experimental values. However, due to the impurities that are introduced during the sampling it is believed these values are off by a factor of 10 or so from the actual water in the loops. No serious work has been attempted to determine quantitatively what happens to the specific resistance of high purity water during sampling.

These results indicate that in all cases the dissolved solids and gaseous impurities are being maintained at very low, almost negligible levels. This indicates that small flow rate clean-up systems and feed and bleed systems both function satisfactorily. The data also shows that pH control has been very effective using the ion exchange-chemical addition method in the ELMO systems.

The methods by which the chemical analyses were obtained have great significance since we are talking about concentrations as low as parts per billion. The metallic impurities were determined by spectrographic[1,2] emission analyses, the dissolved gases by mass spectrometer analyses and the anion impurities and miscellaneous data by wet chemical analyses. When concentrations are referred to as less than some value, the value mentioned is the lowest detectable concentration.

CONCLUSIONS

The results of the experimental work with the out-of-reactor facilities have indicated that,

1. The water pretreatment system is excellent,
2. The over-all loop water clean-up efficiencies are satisfactory,
3. Either ion exchange or feed and bleed clean-up systems are satisfactory.

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(1) Ko, R., Spectrochemical Analysis of Water, HW-48770, January 10, 1957.
(2) Daniel, J.L. and Ko, R., Analysis of High Purity Water by Spectrochemistry, HW-43096, May 7, 1956.

FUTURE WORK

Future work will be concerned with correlating data and preparing a similar report for the 1706 KER in-reactor facilities. Work on the phosphoric acid and lithium hydroxide resins will be completed and the results will be reported. A program will also be initiated to determine the feasibility of removing suspended particulate matter from the water.

ACKNOWLEDGMENTS

The assistance of Coolant Testing Operation, IPD, who operate these facilities as well as Messrs. H. J. Anderson, R. E. Perey and their staffs who performed the analyses is gratefully acknowledged. The help of L. D. Perrigo, Jr., who accumulated a great deal of the required experimental data, is also appreciated.

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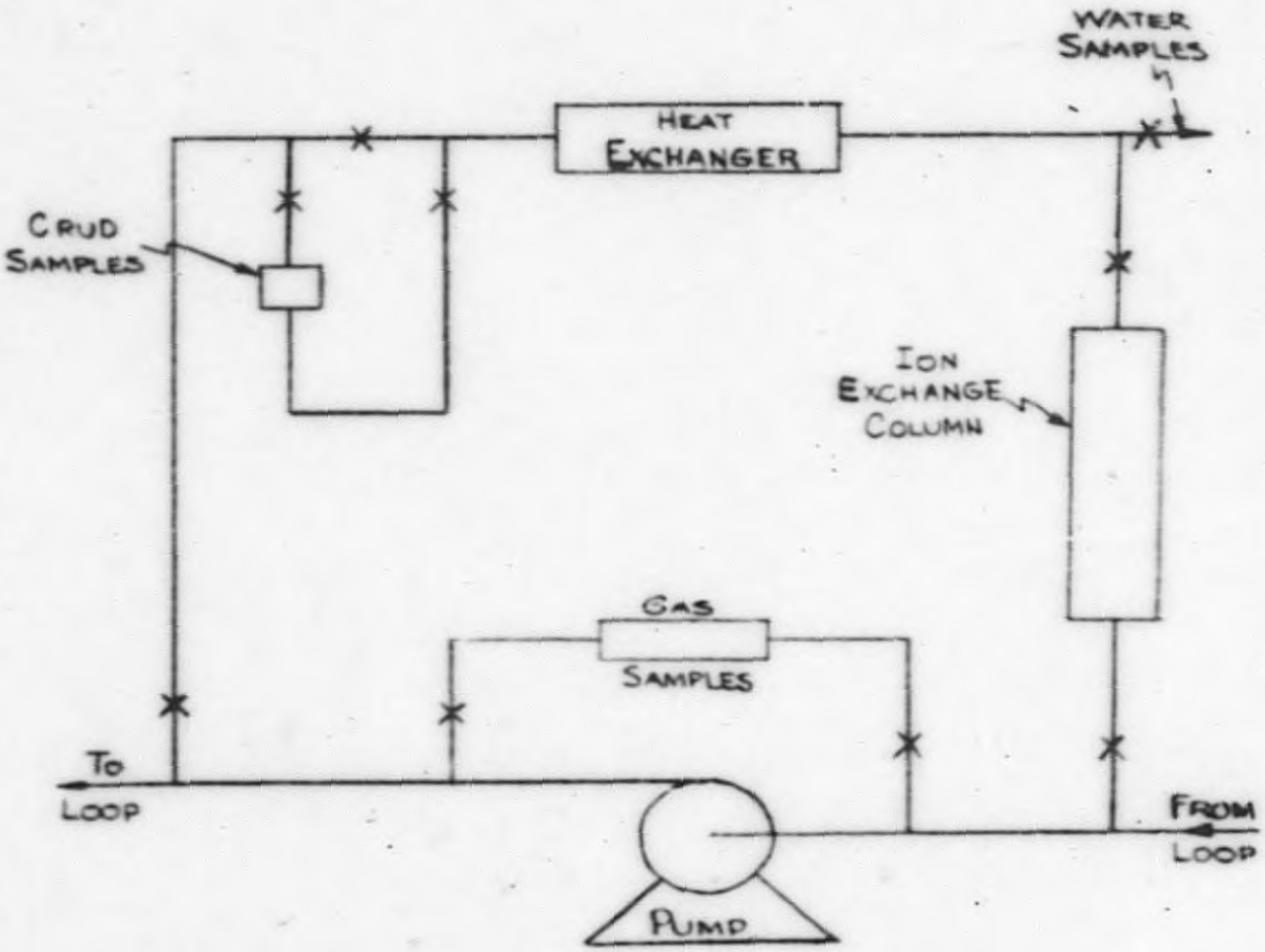

Figure 1. Typical ELMO Clean-up System