Pak. J. Sci. Ind. Res 2005 **48**(3) 174-179

Studies on the Chemistry Control of Some Selected Drinking and Industrial Waters

Riaz Ahmed
Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology (PINSTECH),
P. O. Nilore, Islamabad, Pakistan

(received May 5, 2003; revised February 3, 2005; accepted February 7, 2005)

Abstract. Water is abundantly used in heat exchangers and boilers. Water chemistry control is necessary to avoid corrosion and scaling in industrial water and health hazards in drinking water. Water used in different types of boilers has been analysed and its impact on corrosion and scaling has been discussed. Treated and untreated water samples used in heat exchangers have been analysed and their advantages and disadvantages have been discussed. Heavy and toxic metals in water sources from Rawalpindi-Islamabad area, Pakistan, have been analysed and results are reported and discussed. Water samples of primary and secondary systems of nuclear reactors have been analysed and discussed. Deposits and cruds formed in boilers and heat exchangers have been analysed and reported.

Keywords: water chemistry, water quality, industrial water, drinking water, corrosion in boilers, scaling in boilers

Introduction

Water has great influence on all aspects of human life (Ahmed *et al.,* 2000, 1984; Snoeink and Tenkin1983; Hawkins, 1976). As water is important for human health (Ahmed *et al.,* 2003; ASTM 1981; AWWA, 1971), it is similarly important for industrial applications (AWWA, 1985; Steel and McGhee, 1979)**.** Corrosion alone causes billions of dollars worth of losses to different industries (AWWA, 2001; Butler and Ison, 1979). By maintaining a proper quality control, many billions of dollars can be saved. Corrosion is a complicated process (Kreysa and Eckermann, 1992; Benjamin, 1989) and is different for different types of metals and alloys, thus water quality parameters also vary according to materials and conditions. It is, therefore, important to understand various aspects of corrosion so that proper water quality parameters could be adjusted and maintained. Scaling is the second major problem plaguing the industry (Fair *et el.,* 1966; 1963). A small layer of scales on the boiler and heat exchangers may cause tremendous increase in energy consumption in terms of increased input of oil and gas. Scales formed also cause increase in corrosion. Chemical stabilization of water is necessary to avoid scaling and corrosion problems (Fair *et al.,* 1963). Water quality control to avoid scaling problems is necessary. Fouling and bacterial growth are other problems encountered in the industrial usage of water, but these also lead to scaling and corrosion problems. In the nuclear reactor cooling waters, requirements of water quality control are even more stringent due to the radiation dangers involved (Fangliang, 1994; IAEA, 1993; BNES, 1978).

Different water quality parameters and their effects on corrosion and scaling are discussed in the present study. For this purpose, different water systems and their effects on boilers and heat exchangers were investigated. Quality parameters of the cooling water for nuclear reactors are also discussed. Many types of industrial waters, and corrosion and scale deposits, were analysed and results are reported.

Materials and Methods

Apparatus. The mostly used equipment were pH-meter, potentiograph, titrimeters and 746 VA processor (Metrohm, Switzerland). Other instruments used were polarographic analyzer 174 A with all the relevant electrodes (PAR, USA), conductivity meter (Wescan, USA), flame photometer (Jenway PFP-7, UK), and UV-visible spectrophotometer, ion chromatograph, HPLC and atomic absorption spectrophotometer (Hitachi, Japan). All the glassware used was of Pyrex quality.

Sampling and sample preparation. Water samples were collected in polyethylene or polypropylene bottles. Before the collection of water samples, the bottles were washed with dilute warm nitric acid and rinsed with deionized water. Bottles were again rinsed with the water to be sampled. For the determination of trace metals in water, about 1% $HClO_4$ was added to the bottles before collection of water samples. For the determination of anions, water samples were collected as such and stored at -20 °C and thawed before analysis, or analysis was done immediately after collection.

---

*Author for correspondence; E-mail: riaza@pinstech.org.pk

Physical parameters. Physical tests done on the water samples comprised colour, conductivity, pH, acidity and alkalinity, odour, suspended and dissolved matter, and turbidity, all measured using standard methods (Ahmed *et al.*, 1984; ASTM, 1981).

Determination of cations. Calcium, magnesium, chromium, cadmium, cobalt, nickel, iron, lead, sodium, potassium, zinc and silica were determined using standard methods (Ahmed and Hussain 1996; Ahmed *et al.,* 1996; 1989; 1988; Ahmed and Viqar-un-Nisa, 1989; Ahmed and Stoepler, 1986; Wang, 1985; Welz, 1976).

Determination of anions. Chlorides, carbonates, bicarbonates, phosphates and sulfates were determined using methods already reported (Ahmed *et al.*, 2000; 1999; 1998; Vogel, 1978).

Results and Discussion

Water chemistry considerations. Water chemistry considerations center on four separate concerns: corrosion, scaling tendencies, fouling from suspended matter, and microbiological load. Each one of these is interrelated with each other. These have been briefly defined in the following. Corrosion is defined as an electrochemical alteration of the metal or the physical removal of the metal by force (erosion or cavitations). Scaling is the precipitation of materials exceeding their solubility. Fouling is the precipitation of materials suspended in water. Microbiological fouling occurs when the population of microbial organisms establishes colonies on the surface of the equipment. Some of the harmful effects of these on the water used in industry are: deposits and scales in boilers; stains, discolouration, spots and other defects on industrial products; bad flavours and poor tastes in drinks; corrosion of of boilers and other industrial units; wastage of chemicals; and unsuitably as drinking water. Corrosion is possible to occur at the pH values where the lines (redox potentials) for oxygen reduction or hydrogen evolution lie above the line (redox potentials) for the M/M^{n+} couple. This can be predicted from pourbaix diagram in which potential is plotted versus pH (Pletcher, 1982). From this can be calculated the pH values at which the metal will corrode. Pourbaix diagrams only show the thermodynamic aspects of corrosion. For kinetic aspects at open circuit, or if a lump of the metal is dropped into the same aqueous solution, the metal must take up the corrosion potential, E_{corr}, the potential where no net current flows because the anodic and cathodic partial currents are equal:

$$I_{\frac{M}{M^{n+}}} = I_{\frac{H_2O}{H_2}} = I_{corr}$$

The partial current, I_{corr}, is called the corrosion current and the rate of corrosion estimated from this current and the Faraday's law should be the same as that from weight loss experiments. For example, a corrosion current of 10^{-3} mA cm^{-2} corresponds to a metal loss rate of the order of 10 mg cm^{-2} yr^{-1} (Pletcher, 1982).

Scales formation may be caused by or on account of hard waters, any soluble silicates present, fine suspended particles, salts of Al/Ca/Mg having a tendency to deposit on hot spots even at small concentrations leading to scale formation, formation of deposits due to total dissolved solids, scales deposition due to sulfides/sulfates, and corrosion products deposited as scales. According to the U. S. Bureau of Standards, 1/4" of the scale build-up on heating elements requires 55% more energy to attain the same temperature.

Chemical stabilization is done through the adjustment of pH, [Ca^{++}], and alkalinity of water to its $CaCO_3$ saturated equilibrium. Stabilized water neither dissolves nor precipitates $CaCO_3$, it will neither remove coatings of $CaCO_3$ that may protect pipes against corrosion, nor will it lay down deposits of $CaCO_3$ that may clog pipes.

Chemistry of various categories of water. In Table 1 are given the values of different physicochemical parameters of the boiler water. Lower values of total hardness indicate that formation of scales will be minimum.

Table 1. Physicochemical parameters of boiler water samples

Parameters tested	Sample 1	Sample 2	Sample 3
pH	7.6	7.7	8.2
Conductivity (µmho's/cm)	365	306	534
Total hardness (µg/ml)	88	94	36
Total alkalinity (µg/ml)	220	225	26
Ca-hardness (µg/ml)	65	68	25

In Table 2 are given the levels of different physicochemical parameters of the raw water and treated water. If raw water of this quality is used it will definitely cause problems in the heat exchangers. However, if treated water is used it will not cause problems in the heat exchangers. Thus, it is recommended that only treated water should be used in the heat exchangers.

Table 2. Physicochemical parameters of water for heat exchangers

Parameters tested	Raw water	Treated water
pH	7.3	7.2
Total hardness (µg/ml)	144	nil
Calcium (µg/ml)	92	nil
Alkaliniyy (µg/ml)	160	4.0
Chlorides (µg/ml)	11	3.0
Sulphates (µg/ml)	4.0	nil

In Table 3 are given concentrations of cadmium, lead, copper and zinc. These elements are important from the toxicity and corrosion points of view. These have been measured in two main water sources of Rawalpindi and Islamabad, Pakistan, which are the Simly Dam and Rawal Dam, and Sawan River flowing through this area.

Table 3. Levels of some metals in the water sources for Rawalpindi and Islamabad, Pakistan

Elements (μg/l)	Simly Dam	Sawan River	Rawal Dam
Cd	0.012±0.001	0.21±0.02	0.01±0.001
Pb	3.14±0.32	2.38±0.27	4.06±0.24
Cu	3.34±0.23	4.60±0.28	2.78±0.27
Zn	12.01±1.2	18.92±2.1	9.7±2.8

In Table 4 are given the analytical results of open-well water from Rawalpindi area. Results clearly show that if this water is used in heat exchangers it will cause scale formation. This can also be calculated from the saturation index.

Table 4. Physicochemical analysis of the open-well water from Rawalpindi, Pakistan

pH	7.6
Conductivity (μmho's/cm)	804
Total hardness (μg/ml)	326
Ca (μg/ml)	210
Mg (μg/ml)	116
Total alkalinity (μg/ml)	490
Carbonates (μg/ml)	nil
Bicarbonates (μg/ml)	490
Chlorides (μg/ml)	15
Sodium (μg/ml)	25
Sulphates (μg/ml)	8

Water chemistry of nuclear reactors. Water chemistry of nuclear reactors may be divided into the following main areas: primary system, secondary system, corrosion processes, activation processes and deposits, radiolysis, impurities and sources, water purification of reactors, and quality control.

Corrosion processes in reactors. Corrosion processes in reactors include corrosion due to different reactor materials; environmental conditions such as heat, solutes in water, thermal differences, chemicals, Cl, and radiation environment; H_2 uptake; and corrosion caused by Zr.

Activation processes and deposits. These are related to the development of activation processes due to radioactivity, production of other elements due to nuclear reactions, such as $^{10}B(n, \alpha)$, ^7Li, and production of several fission products, such as tritium, H-3.

Radiolysis. This may involve dissociation of water, such as into H_2, O_2 and H_2O_2 (H^+, OH^-, H, O^-, HO_2^-, etc.); impurities in water getting ionized, such as, Br, Cu, $Br^+ + H \rightarrow Br^{--} + H^-$; and conversion of dissolved nitrogen to ammonia, nitrates and nitrites.

The primary system. The PWR primary system chemistry is complicated (BNES, 1978).

In Table 5 are given the values of lead, copper, chlorides and conductivity in water used as the primary cooling water in the reactor at PINSTECH, Islamabad. These physicochemical parameters mostly cause corrosion.

Table 5. Physicochemical analysis of primary reactor cooling water

Sample	Conductivity (μmho's/cm)	Cl^- (μg/ml)	Cu (μg/ml)	Pb (μg/ml)
R2-1	5.0	nil	0.02	nil
R2-2	5.5	nil	0.018	0.02
R2-3	5.0	nil	0.017	nil
R2-4	4.4	nil	0.009	0.003
R2-5	4.8	nil	0.011	0.002
R2-6	3.4	nil	0.006	0.001
R2-7	6.0	0.2	0.007	nil
R2-8	5.0	nil	0.005	0.002

Conductivity is proportional to the salt contents present in water and it should be ideally minimum. The values reported in Table 5 are within the permissible levels. Similarly, the values of chlorides, copper and lead are also within the limits. Thus, these types of water samples are suitable for reactor.

Chemical shim control. Main aspects of chemical shim control are: reactor control, rods of high cross-section materials, dissolution of a nuclear poison in coolant, provision of better power distribution in the core, chemical shim being better than full rod control, solubility and stability of boron being important, and control of pH done by using LiOH. It has a low neutron capture cross-section and does not form significant radioactive products.

pH control by lithium. H_3BO_3, a weak acid at 25 °C, becomes even weaker at higher temperatures. The ions present and their equilibrium constants have been studied. In selecting a base, it must be noted that Li-7 is produced by the following reaction:

$$^{10}B(n, \alpha)\,^7Li$$

Further, Li-7 has a low neutron capture cross-section and does not form significant radioactive products. Therefore, Li-7 has been selected for alkalinity control by most PWR reactors. The separated isotope is used since naturally occurring lithium contains only 93% lithium-7 and 7% Li-6. The latter isotope undergoes the reaction to form undesirable tritium:

$^{6}\text{Li}(n, \alpha)^{3H}$

KOH may cause formation of oxides and deposits on the core, thus caustic cracking may occur. Li is more compatible with structural materials.

The secondary system. It involves mostly steam generator chemistry. PWR has two closed cycles (primary system and secondary system) linked together. An advantage of this design is that radioactivity occurs only in the primary system. Water chemistry specifications for steam generators have been given (IAEA, 1982). Specifications may vary from plant to plant and also from different suppliers.

Present problems and solutions for the secondary system. Slightly alkaline and reducing systems, and improved chemistry, remove many problems. Major problems are: IGA or SCC, tube/tube support crevices, tube sieving and plugging, caustic deterioration, lead impurities, and corrosion products. Different quality parameters are considered and provided with every reactor by the manufacturer/supplier for the primary and secondary systems (IAEA, 1982).

In Table 6 are given the typical values of crud/sludge usually formed in the secondary systems, which were collected and analysed.

Table 6. Analysis of crud/sludge

Constituents		Concentration
Iron	(F_2O_3)	30.2 %
Silica	(SiO_2)	14.0 %
Zinc	(ZnO)	12.3 %
Copper	(Cu_2O)	11.0 %
Phosphates	(PO_4)	10.0 %
Nickel	(Ni_2O_3)	5.1 %
Lead	(PbO)	0.9 %
Cobalt	(Co_2O_3)	0.7 %
Clacium	(CaO)	0.2 %
Chromium	(Cr_2O_3)	0.2 %

On carefully looking at the results of the crud analysis, it was revealed that corrosion was taking place. Iron, copper, nickel and zinc were produced due to corrosion. Other constituents, such as silica and calcium, may be due to the impurities present in water. Phosphate is usually added to reduce corrosion. These results also show that water quality parameters were not properly adjusted, therefore, it caused corrosion. If properly treated water had been used, this corrosion could have been avoided, and consequently the life of the plant would have been increased.

In Table 7 are given the values of different constituents found in the boiler crust.

Table 7. Analysis of boiler crust

Constituents	Concentration (%, by wt)
CaO	52
SiO_2	5
Fe_2O_3	<0.1
Zn, Cu, Pb, Mn	all <0.01
CO_3 (as CO_2)	39.3
SO_4	2.6

From the analytical results of the boiler crust, it can be said that at this stage no corrosion was taking place, however, corrosion would have initiated if the scales had not been removed. Presently, it is merely the case of scale formation. Water used in the boiler was not properly treated. Therefore, it caused scale formation. This scale formation causes energy losses of more than 50%, and if not removed may cause corrosion and ultimately the boiler may be damaged.

In Table 8 are given the values of some constituents as formed in the heat exchangers of the reactor's secondary system, which were collected and analysed. This scaling caused clogging of pipes.

Table 8. Analysis of scale deposits in heat exchangers

Constituents	Concentration (%)
CO_3	59.4
SO_4	4.0
Cl	0.06

These results also show that untreated water was used in the heat exchangers that caused scale formation, which thus caused clogging of pipes. This scale formation was developed in a short span of time. It was suggested that water should be treated and hardness should be removed. This water may be used in heat exchangers by maintaining water quality parameters. The same plant is using the treated water for the last more than fifteen years and as a result no scaling problems have developed.

Industrial chemical water treatment. After the removal of undesirable impurities from water and adjusting the quality parameters, certain chemical treatments further enhance the life of plants. The types of treatments for different types of plants are given below.

Cooling tower treatment. This can be done by using scale, deposit and corrosion inhibitor, such as polymeric/organic/ phosphate/azole type.

Biocides. Chlorine dioxide (ClO_2) may be used as a biocide. The on-site generation of chlorine dioxide from two non-toxic reagents has proven to be very effective in today's alkaline pH environments, which is effective against all types of biological growth and bacteria. Purobrom tablets (halogenated hydantoin-tableted form), which release an active bromine disinfection species in water, are also used.

Boiler treatment. This can be done by the use of oxygen scavengers, such as sodium sulfite type. Internal boiler water treatment (polymeric/organic/phosphate type) as the primary internal finishing treatment for boilers up to 1000 psi with low hardness feed water, can be effectively done.

Steam/condensate line corrosion inhibitor - (neutralizing amine type). This treatment prevents corrosion in steam and condensate lines by neutralizing acidic conditions and prevents transport of corrosion products to boilers.

References

Ahmed, R. (ed.). 2000. *Proc. Training Workshop Water Chem. and Quality Control,* NCD/L-**121:**1-190, PINSTECH, Islamabad, Pakistan.

Ahmed, R., Durbeck, H.W., Stoeppler, M., Nurnberg, H.W. 1988. Gas liquid chromatographic analysis of methylmercury in fish and its comparison with total mercury. *Pak. J. Sci. Ind. Res.* **31:** 535-540.

Ahmed, R., Hussain, M. 1996. Determination of trace metals in natural waters by differential pulse anodic stripping voltammetry. *Nucleus* **33:** 95-100.

Ahmed, R., Nisa, V. 1989. Simultaneous determination of Cd, Pb, Cu and Zn in different materials using differential pulse anodic stripping voltammetry. *Pak. J. Sci. Ind. Res.* **32:** 639-642.

Ahmed, R., Nisa, V., Qureshi, S.A., Hussain, M., Tanwir, R. 1998. *Quality Control of Drinking and Industrial Water;* Report **116:** 1-30, PINSTECH/NCD, Islamabad, Pakistan.

Ahmed, R., Qureshi, S.A. 2003. Determination of As (III) and As (V) in natural waters using differential pulse voltammetry. *Nucleus* **40:** 13-17.

Ahmed, R., Qureshi, S.A., Hussain, M. 1999. Determination of cyanide in drinking and wastewater by voltammetry. *Nucleus* **36:** 181-184.

Ahmed, R., Stoeppler, M. 1986. Decomposition and stability studies of methylmercury in water using cold vapour atomic absorption spectroscopy. *Analyst* **111:** 1371-1374.

Ahmed, R., Tanwir, R., Qureshi, I. H. 1984. *Chemical Analysis of Surface and Ground Water from Selected Areas of Pakistan,* Report **107:** 1-144, NCD-PINSTECH, Islamabad, Pakistan.

Ahmed, R., Yamin, T., Ansari, M.S. 2003. Monitoring of Cadmium in drinking water by voltammetry. *Nucleus* **40:** 7-12.

ASTM. 1981. *Annual Book of American Society for Testing of Materials (ASTM) Standards, Part-31, Water*, Philadelphia, USA.

AWWA. 2001. *External Corrosion: Introduction to Chemistry and Control*, American Water Works Association, Washington, USA.

AWWA. 1985. *Standard Methods for the Examination of Water and Wastewater*, American Water Works Association, Washington, USA.

AWWA. 1971. *Water Quality and Treatment,* American Water Works Association, McGraw Hill, New York, USA.

Benjamin, M.M. 1989. *Chemistry of Corrosion Inhibitors in Potable Water*, American Water Works Association, Washington, USA.

BNES. 1978. *Proc. International Conf. Water Chem. Nuclear Reactor Systems,* British Nuclear Energy Society, London, UK.

Butler, G., Ison, H.C. 1979. *Corrosion and its Prevention in Waters,* Krieger Publishing Company, USA.

Fair, G.M., Geyer, J.C., Morris, J.C. 1963. *Water Supply and Waste Water Disposal,* John Wiley and Sons, Inc., New York, USA.

Fair, G.M., Geyer, J.C., Okun, D.A. 1966. *Water and Wastewater Engineering*, John Wiley and Sons, Inc., New York, USA.

Fangliang, L.1994. Water *Chemistry of PWR Nuclear Power Plants*, pp. 1-252, Nuclear Power Technology Training Centre of CNNC, Beijing, China.

Hawkins, D.T. 1976. *Physical and Chemical Properties of Water,* Plenum Press, London, UK.

IAEA. 1993. *Coolant Technology of Water International,* Atomic Energy Commission, Technology Report Series No.347, International Atomic Energy Agency, Vienna, Austria.

IAEA. 1982. *Water Chemistry and Corrosion Problems in Nuclear Power Plants,* International Atomic Energy Commission, IAEA, Vienna, Austria.

Khalid, N., Rahman, S., Ahmed, R., Qureshi, I.H. 1987. Determination of lead and cadmium in milk by electrothermal atomic absorption spectrophotometry. *Intern. J. Environ.*

Anal. Chem. **28:** 133-141.

Kreysa, G., Eckermann, R. (eds.). 1992. *DECHEMA Corrosion Handbook: Corrosive Agents and their Interaction with Materials, Carboxylic Acid Esters, Drinking Water, Nitric Acid,* John Willey and Sons, New York, USA.

Pletcher, D. 1982. *Industrial Electrochemistry*, Chapman and Hall Ltd., London, UK.

Snoeink, V. L., Tenkins, D. 1983. *Water Chemistry,* John Wiley and Sons, Inc., New York, USA.

Steel, E.W., McGhee, T.J. 1979. *Water Supply and Sewerage,* McGraw- Hill, Tokyo, USA.

Vogel, I.M. 1978. *Textbook of Quantitative Inorganic Analysis*, Longman, New York, USA.

Wang, J. 1985. *Stripping Analysis: Principles, Instrumentation and Applications,* VCH Publishers, Inc., Deerfield Beach, Florida, USA.

Welz, B. 1976. *Atomic Absorption Spectroscopy*, Verlag Chemie, Weinheim, New York, USA.