Monitoring of Water Chemistry and Corrosion Probability of BAEC TRIGA MARK-II Research Reactor

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Abstract

TRIGA (Training, Research, Isotopes, and General Atomics) reactor is the most widely used non-power nuclear reactor globally. Water is used as a coolant in this reactor. Suitable coolant chemistry and corrosion control are indispensable for the successful operation of any nuclear reactor. This study investigated the physicochemical properties of primary and secondary coolant used in the BAEC TRIGA research reactor (BTRR) and their relationship to the corrosion and scaling tendency. The Langelier saturation index, ryznar stability index and aggressive index were calculated to predict the coolant's scaling and corrosion tendency. The obtained results revealed that the distributed water needs more treatment in context of some minerals in primary water which may leads corrosion or deposition in the primary water distribution system. Secondary coolant is found overall in good conditions and majority of the parameters are within the acceptable ranges. Thus, such an investigation is needed to identify possible contamination sources–ion exchange resin, storage tanks, or pipelines–to ensure coolant quality for the safe operation of BTRR.

Keywords: Reactor coolant, Physico-chemical properties, Corrosion indices, UV-vis spectrophotometer, Atomic absorption spectrophotometer

1. Introduction

Nuclear reactors have made valuable contributions to nuclear power development, basic science, materials development, education, training, and radioisotope production for medicine and industry over 60 years. The TRIGA-reactor is used for training, research, and isotope production. There are more than 50 TRIGA reactors in operation around the world [1]. Regardless of the reactor type, application, composition, or power level, water is used as the core coolant, moderator, and biological shielding in the majority of them. The Bangladesh Atomic Energy Commission TRIGA Research Reactor (BTRR) has been operated since 1986 to steady state power of 3MW [2]. It is a tank type reactor, cooled and moderated by light water, graphite reflected, designed for steady-state, square wave and pulsing with the maximum power level of 852 MW [3].

Coolant chemistry is an essential factor in the safe and reliable operation of nuclear reactor. Water-cooled reactor experience shows that some undesirable effects like corrosion, erosion, or deposition of corrosion products on heat transfer surfaces can occur even under normal operating conditions. Corrosion leads to increase some trace metals concentration in tap water like lead, cadmium, nickel, copper, iron, and zinc. The accumulation of corrosion products inside the pipes can cause plugging and lead to operational difficulties [4]. Water corrosivity or scaling tendency is affected by its physical and chemical properties. Various water quality parameters including pH,

alkalinity, buffer intensity and total dissolved solids can affect corrosion or scales in iron and steel pipes used in water distribution utilities [5]. The components forming scale in saltwater environments are calcium carbonate, calcium sulfate, and magnesium hydroxide. Important factors affect scale formation, such as the concentration of salts, flow velocity, water temperature, and pH of air [6]. Water chemistry of nuclear as well as research reactors can govern six different perspectives, i.e., material integrity, plant radiation levels, deposit build-up, fuel performance, environmental impact, and safety [7].

The cooling system at BTRR has two cooling loops. The primary cooling system is a closed-loop based on demineralized water of specified quality. The secondary cooling loop is based on natural underground water that takes up the preliminary heat through a heat exchanger and disperses it to the atmosphere through cooling tower. The primary coolant is subjected to gamma and neutron irradiation by the core, producing radiolysis species, such as O_2 and H_2O_2, which induce oxidation reactions of dissolving substances within them. It may cause corrosion in the reactor tank components and other undesirable effects like forming compound deposits inside the cooling system, particularly inside the heat exchanger cores, thereby adversely affecting its performance and lifespan [8]. The water stream's kinetic energy causes erosion of pipes and components of the circuit on circuits with forced circulation. During erosion, tiny fractions of these components are mechanically released in the form of particles transported downstream, deposited as sediments, or dissolved in the form of charged particles (cations, e.g.,

Na^+, Ca^{2+}, K^+; anions, e.g., Cl^-, CO_3^{2-}, SO_4^{2-}). The capacity of water for dissolved species in a solution is limited. However, if the amount of dissolved species exceeds the "solubility product" of a specific compound, this compound will precipitate from the water in the form of salts, i.e., scaling formed. The current research aims to measure the reactor coolant's physicochemical properties and its relation to the corrosion and scaling tendency to control and maintain the water chemistry within the required specifications to ensure the reactor system's longevity and performance. Furthermore, three corrosions and scaling forming indices, such as Langelier saturation index (LSI), Ryznar stability index (RSI), and Aggressive index (AI) were measured using the obtained physicochemical data.

2. Materials and Method

2.1 Reagent and instrumentation

Each element's standard solution was prepared immediately by diluting 1000 mg L^{-1} stock solution (Wako Pure Chemicals, Osaka, Japan) before use. Analytical reagent grade chemicals (Merck, Darmstadt, Germany) were used throughout. Digital analytical balance (CP 225 D, Sartorius, Göttingen, Germany), hot plate with a magnetic stirrer (Stuart, Staffordshire, UK), pH meter (Orion 4 star, Waltham, MA), conductivity meter (EC-214, Hanna instrument, Villafranca Padovana PD, Italy), flame atomic absorption spectrometer (AA6800, Shimadzu, Kyoto, Japan), UV-VIS spectrophotometer (UV-3401, Shimadzu, Kyoto, Japan) were employed in the experiment.

2.2 Sampling

Two types (primary and secondary) of water samples were collected from five sampling points; (i) Reactor pool water (RPW), (ii) Primary make-up water (PMW), (iii) secondary make-up water (SMW), (iv) Cooling tower standby water (CTSW) and (v) Bleed offline water (BOLW). They were collected from the BTRR facility in pre-washed LDPE container and stored in refrigerator at 4^oC for future elemental analysis. The physical parameters were measured during the sampling period. The study was carried out for three consecutive years, reported as RY-1 (2017), RY-2 (2018), and RY-3 (2019). The primary water samples were collected on weekly basis, and the secondary water samples were collected once every three months.

2.3 Sample preparation

The digestion procedure for water samples was underway by transferring a measured volume (50 mL) of well-mixed acid preserved water sample to a flask. Then 3.0 mL of HNO_3 and pre-cleaned few boiling chips were added into the flask. The water samples were heated near to boiling and evaporated on a hot plate up to the sample remained 2~3 mL in the flask. After this, the flask was cooled, washed down with deionized water, and filtered through Whatman No. 44 filter paper. A portion of this solution was taken for Cu, Zn, Ni and Co measurements. La_2O_3 solution (2.5 mL) was added for Ca and Mg measurements, while $CaCO_3$ solution (5 mL) was added to measure Fe and Mn in the digested filtered sample solution, mix well and made up

to the marked (volume of 25 mL) with ultrapure water [9]. The samples were doubly filtered to ensure to remove all the fine impurities in it.

2.4 Method validation

To confirm the proposed method's reliability for analyzing the selected metals, standard reference material NIST SRM 1643e (Trace Element in Water) was analyzed by following the same method as followed for water sample analysis. The results are summarized in Table 1. The relative standard deviations (RSDs) were obtained in the range of 3.81-8.39% suggesting that the method was satisfying for quantifying the targeted elements in the water samples. Spike recovery studies of five elements were also done to check the accuracy and quality control (QC) of the method. In the recovery study, a spiked sample was prepared and analyzed in the same manner as the studied samples were analyzed (50 mL sample with the known spiked standard was digested and diluted to 25 mL with ultrapure water and then run by FAAS). The spike recovery was found in the range of 90-93% and the results are summarized in Table 2, indicating that the method was acceptable for analyzing metals in designated water samples.

2.5 Corrosion and scaling forming indices

The commonly accepted indices for corrosion and scale-forming are the Langelier saturation index (LSI), Ryznar stability index (RSI), and Aggressive index (AI). Numerous indices show that there is no single and explicit solution for determining water corrosion and scale-forming. The corrosive tendency of water is a complicated phenomenon, which is not only a function of physical and chemical characteristics of water but also of the water transfer system [10].

2.5.1 Langelier saturation index (LSI)

The Langelier saturation index is basically a way to determine water corrosiveness or scale forming tendency. The LSI is defined as the following expression [11].

$$LSI = pH_A - pH_S \qquad (1)$$

where,

pH_A = Actual pH of water, pH_S = pH at saturation in calcium carbonate = $(9.3 + A + B) - (C + D)$, where, A, B, C, D are the co-efficient that are estimated as; A = (log [TDS]-1)/10, B = $-13.12 \times \log (^0C+273) +34.55$, C = log [$Ca^{2+}$] and D = log [Alk].

In these equations, TDS is the total dissolved solids, expressed in mg L^{-1}; [Ca^{2+}] is the concentration of Ca^{2+} ions expressed as $CaCO_3$ in mg L^{-1} and [Alk] is the total alkalinity given in the equivalent $CaCO_3$ and expressed in mg L^{-1}. According to the LSI value, the corrosion and scaling tendency are shown in Table 3.

2.5.2 Ryznar stability index (RSI)

The Ryznar stability index is expressed using the following equation [12]

$$RSI = 2(pH_S) - pH_A \qquad (2)$$

In equation (2), pH_S and pH_A are of same meaning used in

LSI equation. The corrosion and scaling tendency of water according to different RSI values are shown in Table 3.

Table 1: Result obtained for the standard reference materials (SRM) together with the certified value (μg L^{-1})

SRM	Element	Certified value	Measured value	RSD (%)
NIST SRM 1643e Trace Element in Water	Ca	32300 ± 1100	30688 ± 841	4.99
	Mg	8037 ± 98	7625 ± 158	5.12
	Fe	98.10 ± 1.40	94.36 ± 1.96	3.81
	Mn	38.97 ± 0.45	36.30 ± 0.86	6.85
	Cu	22.76 ± 0.31	20.85 ± 0.80	8.39
	Zn	78.50 ± 2.20	75.46 ± 0.86	3.87
	Co	27.06 ± 0.32	25.86 ± 0.62	4.43
	Ni	62.41 ± 0.69	58.42 ± 0.76	6.39

2.5.3 Aggressive index

The aggressive index was developed to contribute for the selection of proper pipeline for transfer of water in transfer lines of distribution network. It is based on water acidity and solubility of calcium carbonate [13]. This index is calculated using the following equation [14].

$$AI = pH + \log ([Alk][Ca]) \qquad (3)$$

Table 2: Concentration of metals (mg L^{-1}) in samples without and with spike

Element (SMW in RY-2)	Analyzed value without spike	Spike amount	Analyzed value with spike	Recovery (%)
Cu	0.09	0.20	0.27	93
Zn	0.39	0.20	0.54	92
Fe	0.19	0.20	0.36	92
Ni	0.24	0.20	0.40	90

Table 3: Corrosion and scaling tendency of water at different Langelier saturation index (LSI), Ryznar stability index (RSI), and Aggressive index (AI) values [15-17]

LSI Index		RSI Index		AI Index	
Value	Probability	Value	Probability	Value	Probability
LSI = 0	Considered to be neutral	RSI<5.5	Highly scale forming	AI<10	High water corrosion
LSI<0	Corrosion tendency	5.5<RSI<6.2	Relative scale forming and corrosive	10<AI<12	Moderate water corrosion
LSI>0	Scaling tendency	6.2<RSI<6.8	Balanced	AI>12	Lack of water corrosion
		RSI>8.5	Corrosive		

In equation (3), [Alk] is total alkalinity (mg L^{-1} as calcium carbonate) and [Ca] refers to calcium hardness (mg L^{-1} as

calcium carbonate). At different AI values, the corrosion tendency is shown in Table 3.

3. Results and Discussion

3.1 Physical characteristics

The pH values were 5.1-7.6 and 6.2-7.8; EC were 0.3-0.9 μScm^{-1} and 102-293 μScm^{-1}; TDS values are 0.20-0.45 mgL^{-1} and 51-147 mgL^{-1} for the primary and secondary cooling water respectively. However, the acceptable ranges of pH, EC and TDS for the primary and secondary cooling water are 5.0-6.5 and 6.0-8.0; <1.0 μScm^{-1} and <200 μScm^{-1}, 1-3 mgL^{-1} and <110 mgL^{-1} respectively [18]. The result showed that the primary water's pH values slightly deviated from the recommended value (Fig. 1a); however, the secondary water pH value was within the permissible range. The primary coolant's electrical conductivity was within the safety range of (0.2-1.5 μScm^{-1}) in RY-1 and RY-2, and RY-3, as shown in Fig. 1b. However, in secondary coolant, the measured EC values were also within the recommended range. The TDS values were below the recommended ranges of the set for primary and secondary cooling water.

3.2 Chemical characteristics

The values of total hardness (TH) of primary water were found 10±1.10 mg L^{-1} in the reporting period RY-3; however, no hardness was found in RY-1 and RY-2 (Table-4). In contrast, the secondary water's lowest TH values were found in RY-3 as 55±8 mgL^{-1} and the highest in RY-2 as 120±28 mgL^{-1}. The TH values for both the water were within the recommended value of <20 mgL^{-1} and <300 mg L^{-1} for primary and secondary cooling water [19]. The total alkalinity (TA) values of the primary water also measured by titration method were in the range of 5.5-10.5 mg L^{-1} whereas, 45-106 mgL^{-1} was observed in secondary coolant during the reporting period (Table-4). The TA values for secondary cooling water were below the acceptable range of <300 mgL^{-1}. However, there is no suggested limit for total alkalinity for primary cooling water in IAEA guidelines [19].

3.3 Anion concentration in water samples

The anionic concentrations of the primary and secondary coolant water samples were also measured and summarized in Table 4. The Table shows that the Cl$^-$ concentration in primary water is slightly higher than the standard value in all the reporting year. It may be due to the high chlorine dosing used during the preliminary water treatment or degradation of the anion exchange resin used for water treatment. The NO_3^- concentration was slightly higher in RY-2. The concentration of SO_4^{2-} was below detection limits in all of the reporting years in primary water and the PO_4^{3-} concentration was found within safety limit for primary water as well (Table 4). However, the anions concentration for secondary water is within the safety limit in all the years.

3.4 Metal ion concentration in water samples

The metal ion concentrations measured in the primary and secondary cooling water samples in different years are

shown in Fig. 2, including the recommended values [18-19]. This study revealed that among the investigated metals, concentrations of Ca^{2+}, Mg^{2+} and Fe^{2+} were higher than the recommended values in every year in primary water (Fig-1(a)). It might be due to the degradation of cation exchange resin's adsorption capacity or the lack of proper treatment of supplied water before entering the deionizer. The other metal concentrations were relatively safe, according to the recommended values. In secondary water, all the metals concentrations were within the acclaimed level every year except for Ca^{2+} and Mg^{2+} in RY-1 (Fig. 2(b)).
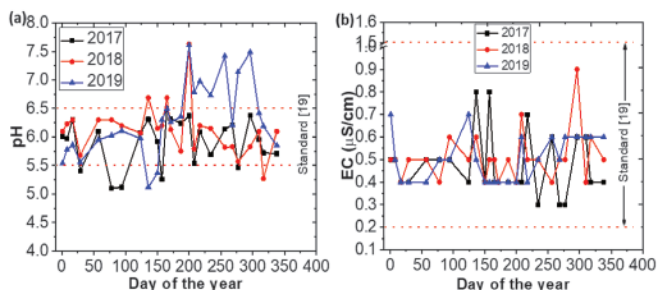
Fig. 1: Variation of (a) pH and (b) Electrical conductivity values in the primary coolant water
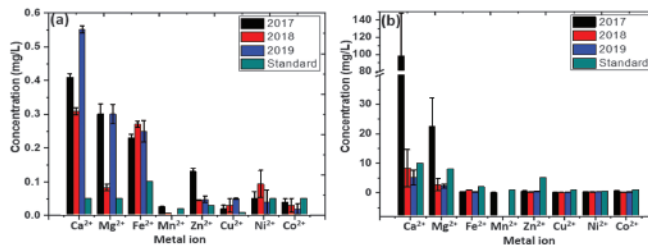
Fig. 2: Metal ion concentrations (average ± std.) of (a) primary and (b) secondary water with recommended value

3.5 Role of different indices on reactor water

The three different indices LSI, RSI, and AI values of primary and secondary coolant water were measured by using the equation (1), (7), (8) and the mean values of those indices are shown in Table-5. From the obtained LSI values of primary water, it could be said that the water was corrosive in nature every year (Table-3). The RSI and AI indices values also showed the corrosive tendency of primary water. In contrast, for the secondary water, the LSI index value was -0.03 to -2.83 among the samples each year, which indicated that the water had corrosive tendency according to the probability index value (Table-3). The RSI and AI value of secondary water was also supported that the water had a moderate corrosion tendency based on Table-3. However, in the year 2018, a detail inspection of reactor

Table 4: Anionic concentration with total hardness (TH) and total alkalinity (TA) of different water samples of research reactor in various years (mgL^{-1})

Anion	Primary water				Secondary water			
	RY-1	RY-2	RY-3	SD [19]	RY-1	RY-2	RY-3	SD [19]
Cl^-	0.32±0.05	0.19±0.01	0.26±0.09	<0.05	0.52±0.10	0.72±0.05	0.40±0.03	6-10
NO_3^-	BDL	0.10±0.08	0.13±0.01	< 0.05	0.48±0.17	1.6±0.80	1.5±0.70	<10
SO_4^{2-}	BDL	BDL	BDL	< 0.1	BDL	2.0±0.27	0.23±0.19	<10
PO_4^{3-}	BDL	0.32±0.13	N.D	< 1.0	0.19±0.15	3.50±0.5	1.70±0.63	<15
TH	BDL	BDL	10±1.10	<20	101.0±29	120.0±28	55.00±8.0	<300
TA	5.50±0.71	6.00±2.83	10.50±2.10	-	59.00±24	106.0±24	45.00±4.1	<300

BDL = Below Detection Limit. Minimum detection limit for NO_3^-, SO_4^{2-} and PO_4^{3-} is ≤0.10 mgL^{-1}

pool liner and reactor tank components has been conducted by IAEA experts. Inspection method includes visual inspection by underwater radiation protective camera as well as the negative putting impression process for corrosion sign and swelling identification. Inspection result of the reactor tank has been found in good condition.

Table 5: Stability and scaling indices (mean value) of primary and secondary water in different years

Indices	Primary water			Secondary water		
	RY-1	RY-2	RY-3	RY-1	RY-2	RY-3
LSI	-4.43	-4.91	-4.66	-0.03	-1.93	-2.83
RSI	14.73	16.21	15.58	7.54	11.17	12.50
AI	6.76	6.76	7.01	11.40	9.99	9.11

4. Conclusion

In summary of the obtained result, it emerged that some metal ions concentration of primary water was slightly crossing the critical maximum levels. In contrast, the other metals and anion concentrations were within the safety level. On the other hand, metal ions like Ca^{2+}, Mg^{2+} of secondary water crossed the permissible operation standard level in RY-1, whereas the other ion concentrations were within the allowable limit. Moreover, according to the measured corrosion indices values, it has been suggested that the reactor's cooling water system is most likely facing the corrosion problem together with scaling, encrusting and fouling. It may be caused by the degradation of the ion exchange resin and the water services lines that may be deteriorated due to aging. That is why it should be taken care of with proper steps such as adequate groundwater

treatment, ion exchange resin changes, replacement of the water supply pipes, etc. and strong monitoring regarding these parameters for optimal operation and longevity of the reactor. Although, detail inspection of reactor pool liner and reactor tank components result has been found in good condition with no sign of corrosion or swelling.

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