Potential Candidates to Replace the Hydrazine as an Oxygen Scavenger in the Secondary Water System of Pressurized Water Reactor

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1. Introduction

One of the major objectives and roles of secondary water chemistry control in pressurized water reactor is to ensure the secondary coolant system components integrity, especially steam generator (SG), to prevent leakage of radioactive contamination from the primary to secondary systems and to maintain the heat transfer efficiency for steam generation [1]. Degradation of the secondary system materials is affected by many water chemistry parameters such as pH, conductivity, dissolved oxygen concentration, and impurity contents [2]. Especially, dissolved oxygen is significantly managed because it accelerates the FAC of carbon steels and the stress corrosion cracking of SG tubing [2]. Dissolved oxygen concentration is controlled by hydrazine addition as a deoxidizer from the rear of the condenser system.

Hydrazine (N_2N_4) reduces the corrosion rates of metals through three reactions as described by Mahal et al [3]. The first reaction is that with oxygen as shown in equation (1), producing nitrogen and water. Although the reaction has a theoretical ratio of 1 between hydrazine and oxygen, the amount of hydrazine actually needs to be 2-3 times that of oxygen to remove entirely [4].

$$N_2H_4(aq) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$$
 (1)

The reaction rate of oxygen with hydrazine has been estimated as a quasi first order reaction with reaction orders of 1 and 0.5 for hydrazine and oxygen, respectively, as shown in equation (2). However, these reaction order can be different, depending on the nature of the metal surfaces facilitating the reactions.

$$-dC_{\rm N2H4}/dt = -dC_{\rm O2}/dt = kC_{\rm N2H4}C_{\rm O2}^{0.5}$$
(2)

Where, C_i and k are concentration of species i and rate constant, respectively. Here, rate constant k has been demonstrated to be temperature dependent according to the Arrhenius equation as shown in equation (3).

$$k = k_0 \exp(-E_a/RT) \tag{3}$$

The second reaction is the thermal decomposition of hydrazine as shown in equation (4), producing ammonia and nitrogen.

$$3N_2H_4(aq) \rightarrow 4NH_3(l) + N_2(g) \tag{4}$$

This reaction occurs much slower and can in the presence of oxygen be considered negligible because reaction rate constant for oxygen removal is about 260 times, comparing that in equation (1). The third corrosion inhibiting reaction of hydrazine is the reduction of hematite to magnetite as shown equation (5). The hydrazine can promote the formation of a more protective passive films on steel surface through this reaction because magnetite layers are generally more stable than hematite (except against FAC).

$$N_2H_4(aq) + 6Fe_2O_3(s) \rightarrow N_2(g) + 2H_2O(l) + 4Fe_3O_4(s)$$
 (5)

The reaction kinetics for the passivating reaction could not be identified from the literature, but might be slow comparing to the oxygen scavenging reaction in equation (1).

However, hydrazine has been classified as a toxic substance with very high concern because it may cause the health problems such as cancer to humans and animals. European Chemical Agency has labelled hydrazine as a hazardous substance since 2011 and strictly regulated the industrial use with a limit less than 1 ppm in EU. The use limit is restricted within 0.01 - 1 ppm range depending on the industry. Especially, the inhalation exposure limit is limited as shown in Fig. 1.



Fig. 1 Limit concentration of inhalation exposure for human and animals [2]

The Korean Ministry of Environment also designated hydrazine as a human hazardous substance in April 2022 and recommended that it be used industrially at a concentration less than 1% [5]. However, this regulatory limit is expected to be changed to U.S. and European limit in near future.

Therefore, the domestic nuclear industry has to select alternatives to replace hydrazine, evaluate the compatibility of secondary system materials, and secure data for regulatory.

2. Hydrazine Alternatives

Efforts to find a hydrazine (HZ) alternative are still ongoing by a lot of researchers, but diethylhydroxylamine (DEHA), carbohydrazide (CHZ), methlethyl-ketoxime (MEKO), ascorbic acid (AA), hydroquinone (HQ) hydrogen have been reviewed as a possible candidate. In addition, methanol and hydrogen have been reviewing.

Fig. 2 shows the hazardous limit of human health and environment for hydrazine and its alternatives. LD50 and LC50 mean the inhalation dose in air and concentration in water, respectively, that kills 50% of the test animals during the observation period. All alternative substances show higher LD50(Rat) value than hydrazine. In addition, DEHA, CHZ, MEKO and AA present about 100 times of LC50 comparing to hydrazine. However, LC50 of HQ has lower value by 1/10 than that of hydrazine [6].



Fig. 2 Hazardous limit of human health and environment for hydrazine and its alternatives

In addition to these human and environmental toxicity data, system material corrosion, oxygen scavenging performance, impact on chemistry and cost & supply were additionally considered as summarized in Table 1. Finally, DEHA and CHZ were selected as a potential candidate through EPRI hydrazine alternatives workshop in 2019.

Table 1. Laboratory evaluation of hydrazine alternatives by Ontario Hydro (now OPG) [7]

Test	Control	А	В	С	D	E
Agent	HZ	DEHA	HQ	MEKO	CHZ	lsoAA
Conc. Ppm	45-100	40-200	170-460	290-315	40-100	400-800
Residual DO, ppb	25-40	4-16	3-10	75-90	20-30	20-30
Agent t- 1/2,d	6-8	6-8	12-16	>100	13	3-11
pH stability	stable	stable	stable	unstable	stable	Stable
Corrosion µm/yr, CS Monel 400	45 None	76 None	530/pits None	45/pits None	69/pits None	63/pits None
Analytical	UV-Vis	IC/GC	GC	IC/GC	IC/GC	GC
Envir. Criteria, ppb	100	100	17	4800	19,000	1E5
LD50, rat, ppm	<100	>2000	400	3500	>5000	NA

3. Diethyl hydroxylamine (DEHA)

N-N-Diethyl hydroxylamine [DEHA, $(CH_3CH_2)_2NOH$] is an organic compound with various applications such as polymerization inhibitor, color stabilizer, corrosion inhibitor, antiozonant and radical scavenger. DEHA reduces dissolved oxygen according to the reaction as shown in equation (6) [8]. The actual reaction mechanisms for DEHA with oxygen are quite complicated and include several steps. In addition, the theoretical ratio of DEHA to oxygen has been estimated to be 1.24, but that in equation (6) shows a ratio of 0.44.

$4(CH_3CH_2)_2NOH(aq)$	+	$9O_2$	\rightarrow	8CH ₃ COOH(aq)	+
$2N_2(g) + 6H_2O(l)$					(6)

DEHA reacts with iron oxides as shown in equation (7) & (8), and has been considered to passivate steels [9].

(CH ₃ CH ₂) ₂ NOH	+	6Fe ₂ O ₃	\rightarrow	CH ₃ CH=NOH	+
$CH_3CHO + 4Fe_3O$) ₄ +	H ₂ O		(7)
(CH ₃ CH ₂) ₂ NOH	+	12FeOOH	\rightarrow	CH ₃ CH=NOH	+
$CH_2CHO + 4Fe_2O$)4 +	7H ₂ O		(8)

The reaction products of DEHA undergo subsequent reactions and the final degradation products

acetaldehyde, dialkyl amines and acetaldoxime acetic acid. Thus, the reaction products of DEHA may either increase (for diethylamine) or decrease (for acetic acid forms) the pH of the coolant. However, the final degradation products should include carbon dioxide and decrease the pH.

Fig. 3 shows the modeled reaction of oxygen and DEHA and HZ, respectively, in the feedwater and condensate train. Even though DEHA with 2.7 times more concentration of HZ is added, the oxygen scavenging performance of DEHA decreases with 1/5 comparing that of HZ. This indicates that the oxygen scavenging performance deteriorates and it can accelerate the corrosion of system materials. However, the corrosion data of carbon steel and copper shown in Fig. 4 is quite different from these modeled results. This might be because the corrosion rate is decreased due to pre-passivation layer as shown in Fig. 5. That is, use of DEHA increases corrosion rate of carbon steel in new nuclear power plant, but decreases that in operated nuclear power plant.



Fig. 3 Modeled reaction of oxygen and, HZ and DEHA in the feedwater and condensate train [7]



Fig. 4 Corrosion of carbon steel and copper in the condensate system [7]



Fig. 5 corrosion of pre-passivated and as-received carbon steel samples [7]

4. Carbohydrazide (CHZ)

Carbohydrazide is the dihydrazide of carbonic acid and can react with oxygen directly [4,10]:

$$(\mathrm{NH}_2\mathrm{NH})_2\mathrm{CO} + 2\mathrm{O}_2 \rightarrow 2\mathrm{N}_2 + 3\mathrm{H}_2\mathrm{O} + \mathrm{CO}_2 \qquad (2)$$

and indirectly through hydrolysis to hydrazine and carbon dioxide:

$$(NH_2NH)_2CO + H_2O \rightarrow 2N_2H_4 + CO_2$$
(3)

$$2N_2H_4 + 2O_2 \rightarrow 4H_2O + 2N_2 \tag{4}$$

Carbohydrazide is relatively stable at or near room temperature and passivates Fe by forming protective passive oxides as;

$$12Fe_2O_3 + (NH_2NH)_2CO \rightarrow 8Fe_3O_4 + 3H_2O + 2N_2 + CO_2$$
(5)

However, since hydrazine is produced as a consequence of carbohydrazide decomposition at the temperature higher than 125°C, shown in reaction (3), carbohydrazide will likely be a possible option as an alternative during power operation.

Fig. 6 shows the modeled reaction of oxygen and CHZ in the feedwater and condensate train. Even though the concentration of CHZ needs more 1.4 times content than that of HZ to eliminate oxygen, its oxygen scavenging performance is better than that of DEHA. Furthermore, it is expected that CHZ has advantages in point of producing the same chemical waste with HZ.

Gaseous byproducts such as nitrogen and carbon dioxide is produced during the decomposition process of CHZ. However, it is expected that the effect of nitrogen and carbon dioxide is negligible because these are low solubility in PWR secondary condition. In addition, inactive gaseous byproducts can be eliminated through vacuuming process at deaerator and condenser.



Fig. 6 Modeled reaction of oxygen and CHZ in the feedwater and condensate train [10]

5. Summary

This paper reviews the characteristics of DEHA and CHZ as potential hydrazine alternative chemicals for the PWR secondary application. It is clearly evident that DEHA and CHZ show the sufficient effective capability for removing oxygen and thus lowering the ECP of steel components that eventually enhances the formation of protective Fe_3O_4 oxide layer for minimizing the corrosion degradation of steel components, without significant negative impacts on the PWR secondary water chemistry.

Nevertheless, in order to apply at NPPs, more systematic experimental efforts are required to optimize the DEHA or CHZ, such as applying concentration, injection rate, injection point, O_2 analysis, corrosion performance, decomposition kinetics, etc.

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