Evaluation of Hydrazine Alternatives as Oxygen Scavenger in PWR Secondary Systems

Energy Transformation Research Laboratory
Central Research Institute of Electric Power Industry (CRIEPI)

Dr. Yudai Yamamoto
yamamoto3758@criepi.denken.or.jp

NRC Workshop on Structural Materials: Research for Beyond 80 Years
October 2, 2024

CRIEPI
Central Research Institute of Electric Power Industry

PWR Secondary Water Chemistry

- All Volatile Treatment (AVT)
  - standard water chemistry for PWR secondary system
  - ex.: N_2H_4 (oxygen scavenger) + NH_3 (pH controlling agent)

- Hydrazine N_2H_4
  - simple reaction products (H_2O, N_2, NH_3)
  - almost essential for PWR operation, **especially in Japan**

    Secondary Water Chemistry Guidelines for Pressurized Water Reactors: 2020, Atomic Energy Society of Japan.
  - highly harmful
    - toxic
    - carcinogenic
    - environmentally toxic

Regulatory trends on hydrazine

- Harmful chemicals are gradually regulated in a global framework
  - such as Strategic Approach to International Chemicals Management (SAICM)

- REACH (Registration, Evaluation, Authorization and restriction of CHemicals)
  - EU regulation addresses production and use of chemicals
  - hydrazine… listed as "**substances of very high concern (SVHC)**" in 2011

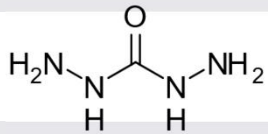
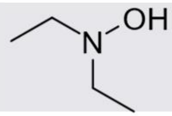
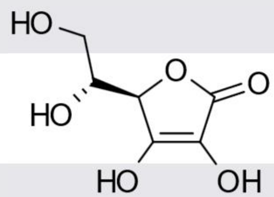
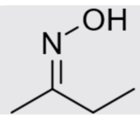
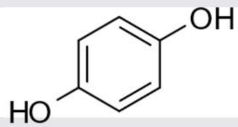
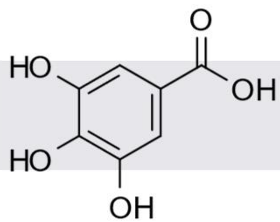
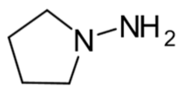
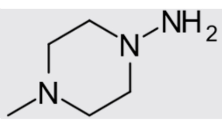
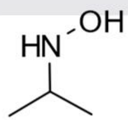
Hydrazine may become hard to use/obtain, although the details and timing of the regulations are unclear.

Hydrazine alternatives should be ready for use before that

Outlines:
Research on hydrazine alternatives in CRIEPI

- Prepare the data to determine promising hydrazine alternatives
  - Literature review on hydrazine alternatives
  - Basic studies to obtain data not available in the literature review
    - Reaction rates
    - Reaction products
    - Ability to ensure reducing environment … in progress (measuring corrosion potential)

Candidates of hydrazine alternatives found in literature review

Name	Abbreviation	Structural formula
(Hydrazine)	(Hz)	H_2N-NH_2
Carbohydrazide	CHz	
N,N-Diethylhydroxylamine	DEHA	
Erythorbic acid	EA	
Methylethyl ketone oxime	MEKO	
Hydroquinone	HQ	
Gallic acid	GA	
1-Aminopyrrolidine	1AP	
1-Amino-4-methylpiperazine	1A4MP	
N-Isopropylhydroxylamine	IPHA	

Summary of literature review

Abbr.	LD_{50}* / mg kg^{-1}	Carcinogenicity	Experience on PWR	Remarks
Hz	59 (mouse)	suspected	YES	- maybe banned
CHz	120 (mouse, intravenous)	not stated	YES	+ many PWR experiences - relatively high toxicity - produces hydrazine by degradation
DEHA	2190	not stated	YES	- increased cation conductivity in PWR experience
EA	18000	not stated	NO	+ food additive (safe for human)
GA	5000 (rabbit)	not stated	NO	
1AP	409 (unknown original source)	not stated	NO	- insufficient information - few applications even in general boilers - hard to obtain (1AP and IPHA)
1A4MP	unknown	not stated	NO	
IPHA	unknown	not stated	NO	
MEKO	1000 (mouse)	suspected	NO	- hard to say safer than hydrazine (suspected carcinogenicity)
HQ	298～390	suspected	NO	

* LD_{50} is the dose of a substance that is lethal to 50% of a test population. Oral intake for rats unless otherwise noted

Measuring oxidation reaction rate constants

- Oxidation reactions are considered as second-order reactions

  O_2 + S → Product

- Concentration of oxygen scavenger [S] is assumed to be in excess of dissolved oxygen concentration [DO]

  [S] >> [DO]

- Reaction rate constant *k* is analyzed as a pseudo-first-order reaction

$$k = \frac{1}{\tau[\mathrm{S}]} \ln \frac{[\mathrm{DO}]_{\mathrm{in}}}{[\mathrm{DO}]_{\mathrm{out}}}$$

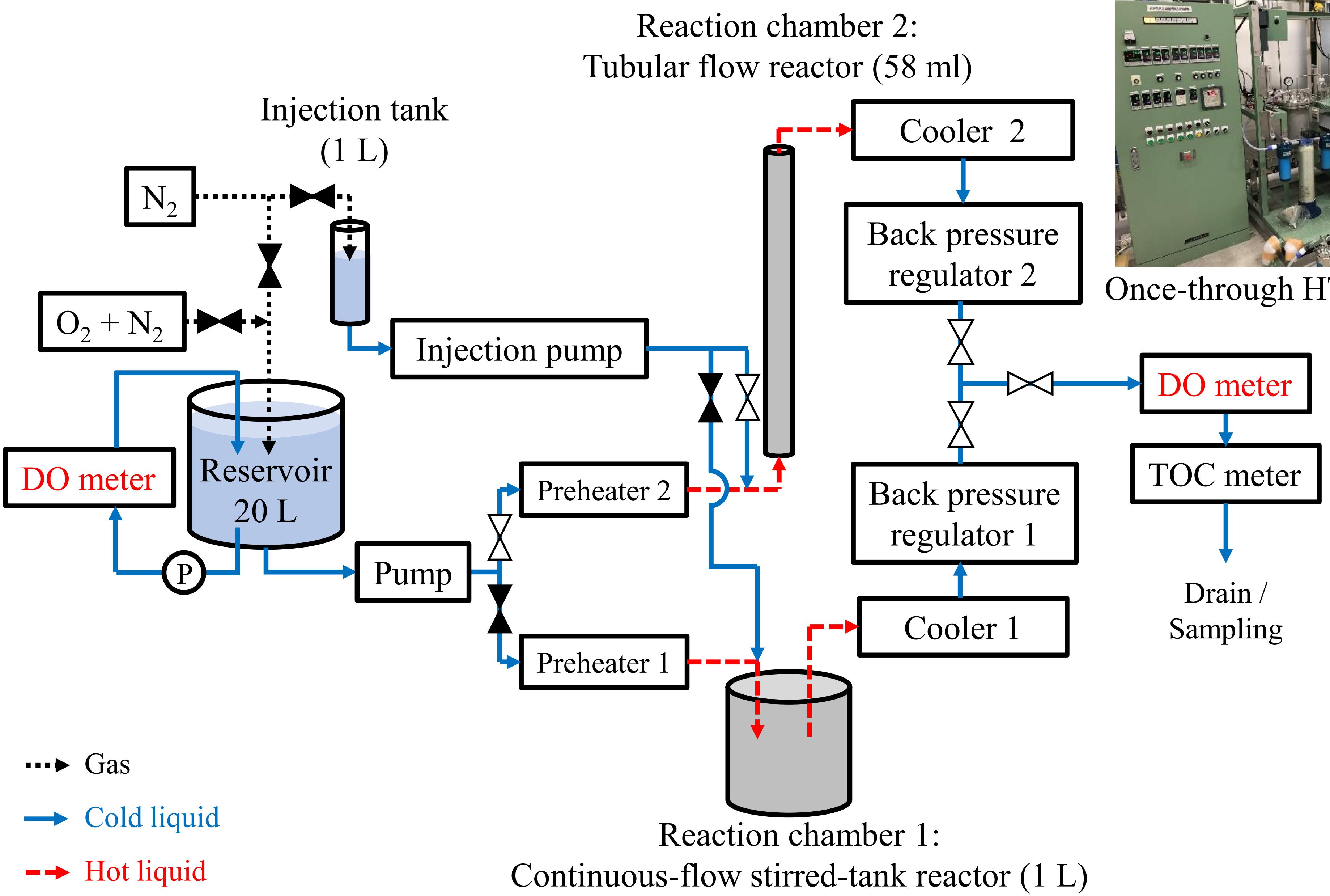
residence time τ = reactor volume V / volumetric flow rate Q

- Temperature dependence of *k* is analyzed by Arrhenius equation

$$\ln k = \ln A - \frac{E_{\mathrm{a}}}{RT}$$

A: frequency factor [s^{-1}]
E_a: activation energy [J mol^{-1}]
R: gas constant [J K^{-1} mol^{-1}]
T: absolute temperature [K]

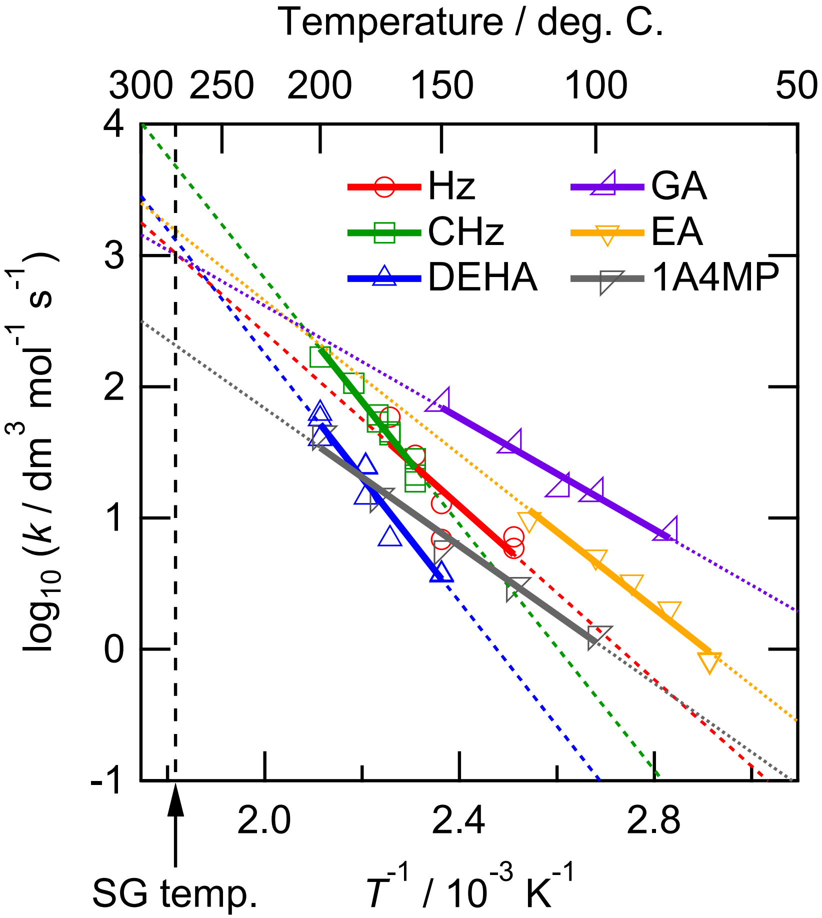
Reaction rate evaluation equipment



Once-through HT&HP boiler

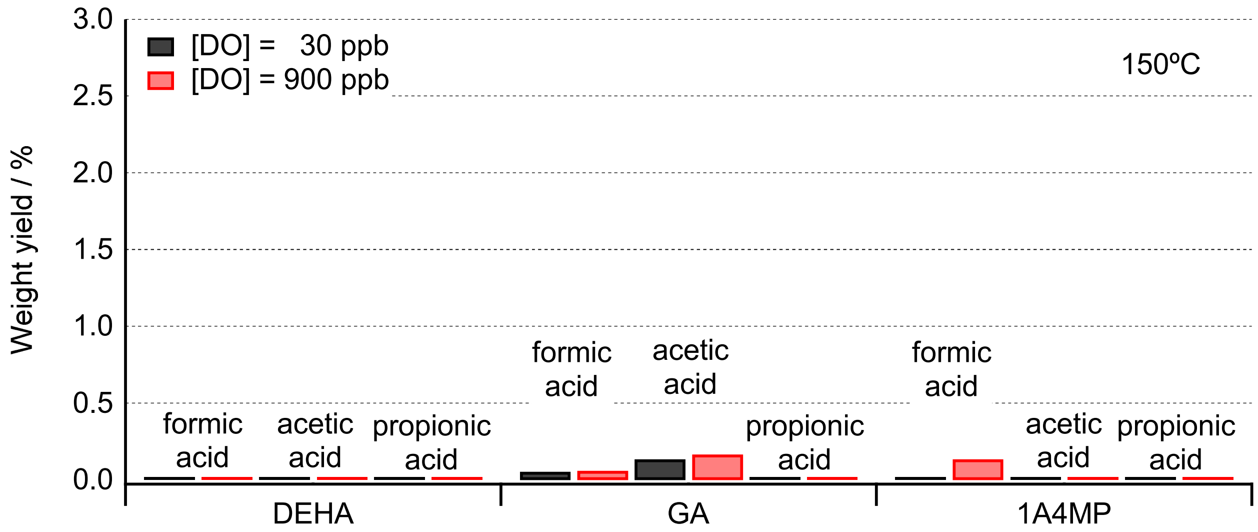
Summarized evaluation results of *k*

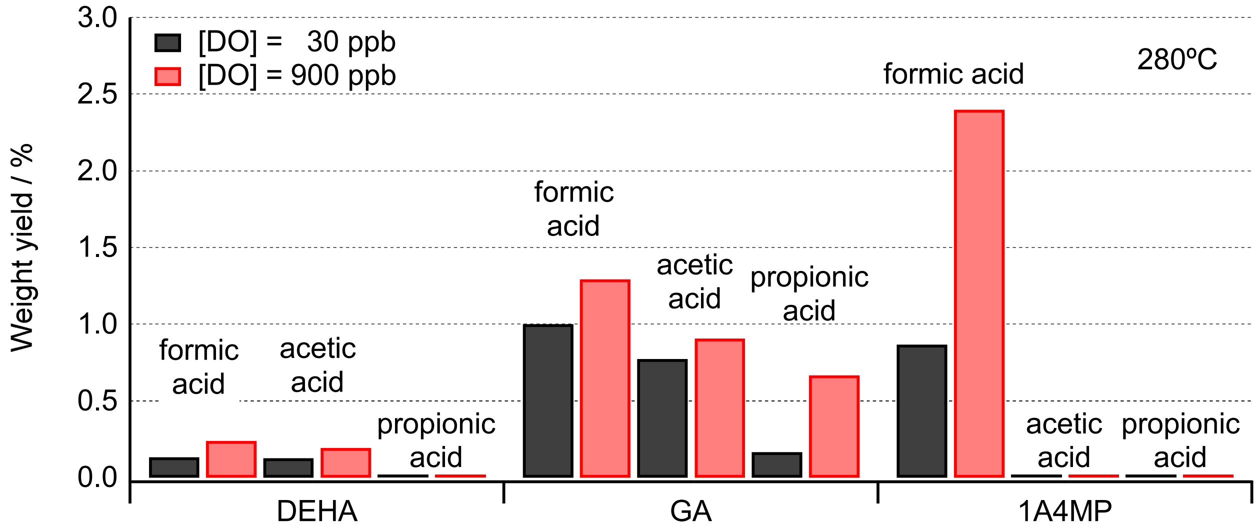
- Evaluated multiple substances using same equipment and conditions
- The reaction rate of 1A4MP at SG temperature appears to be slower
- Fast reaction rates of GA and EA at room temperature



Examples of degradation products evaluation

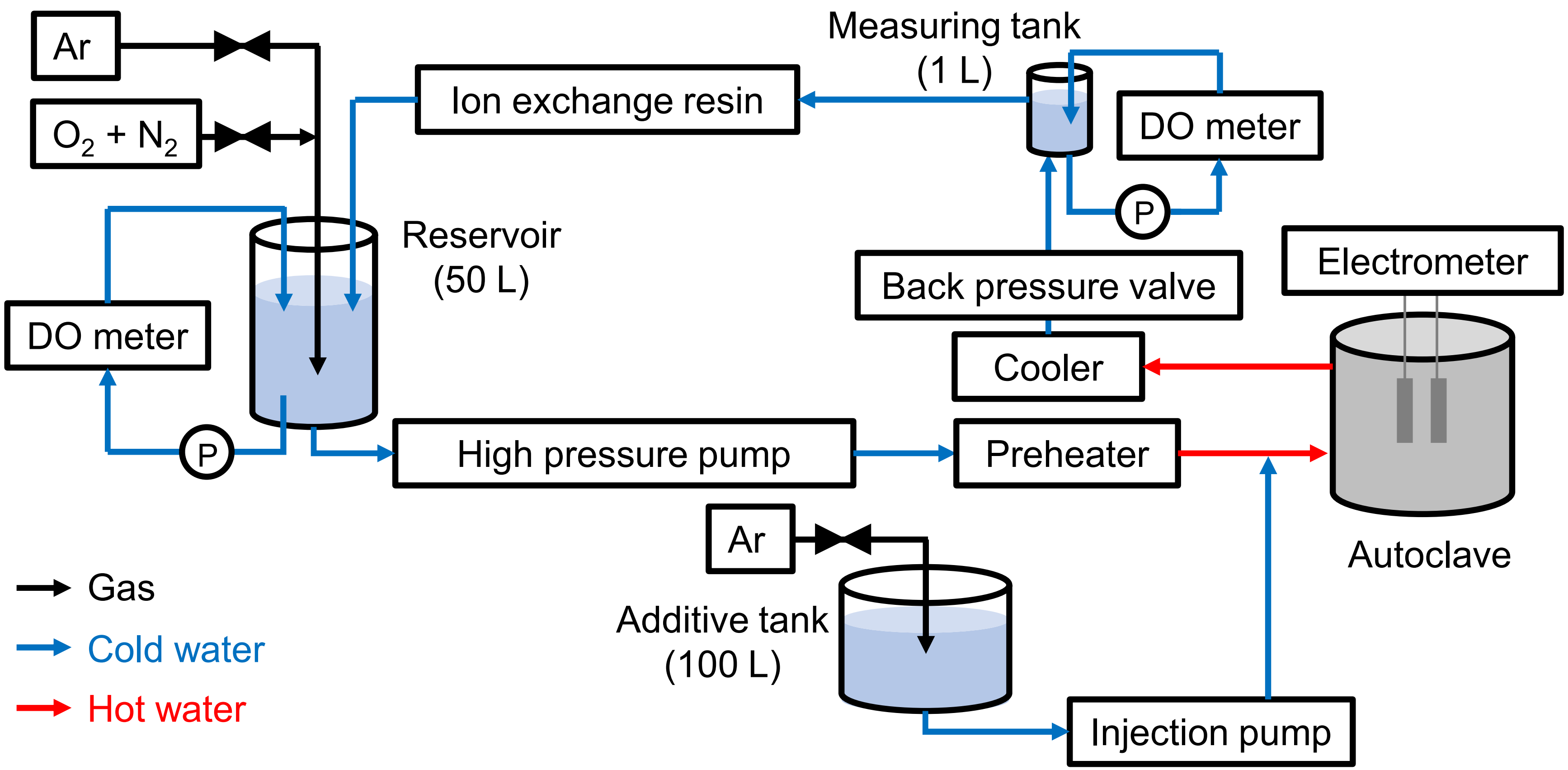
- Focused on carboxylic acids, which may accelerate corrosion
  - Formic acid (C1)
  - Acetic acid (C2)
  - Propionic acid (C3)
- DEHA produces less carboxylic acid
- 1A4MP only produces more formic acid
- In all cases, carboxylic acid production increases under high DO conditions
  - Formic acid production from 1A4MP is particularly significant





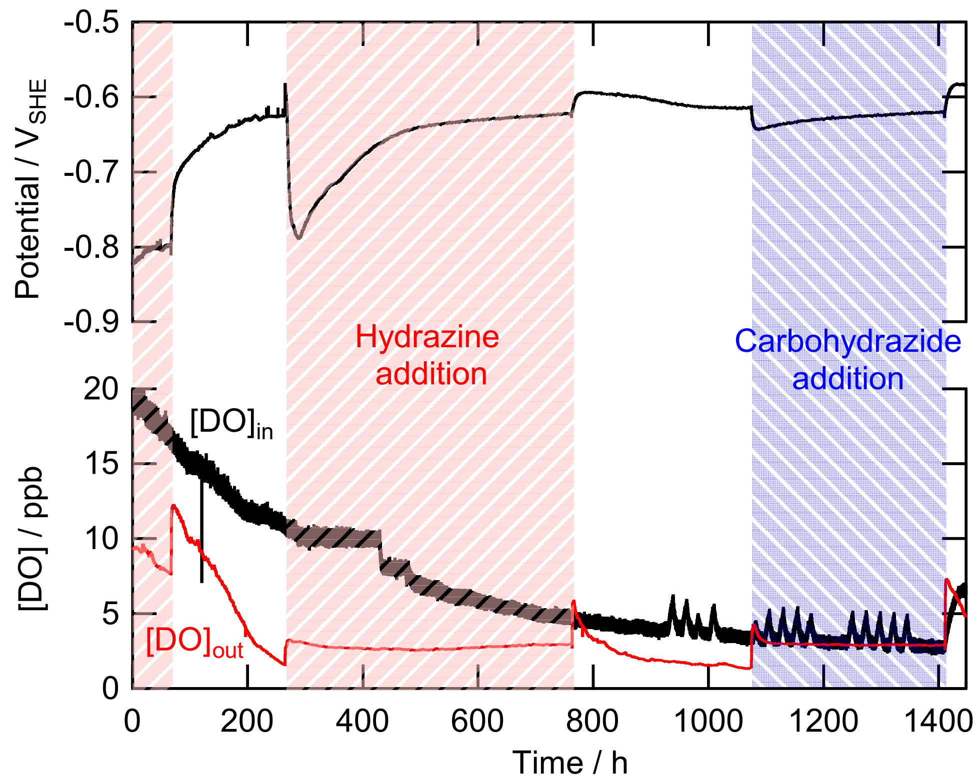
Corrosion potential evaluation equipment

- HT&HP water loop
- Working electrode: SUS405 (SG tube support plate material)
- Reference electrode: Ag/AgCl (0.1 M KCl, external)



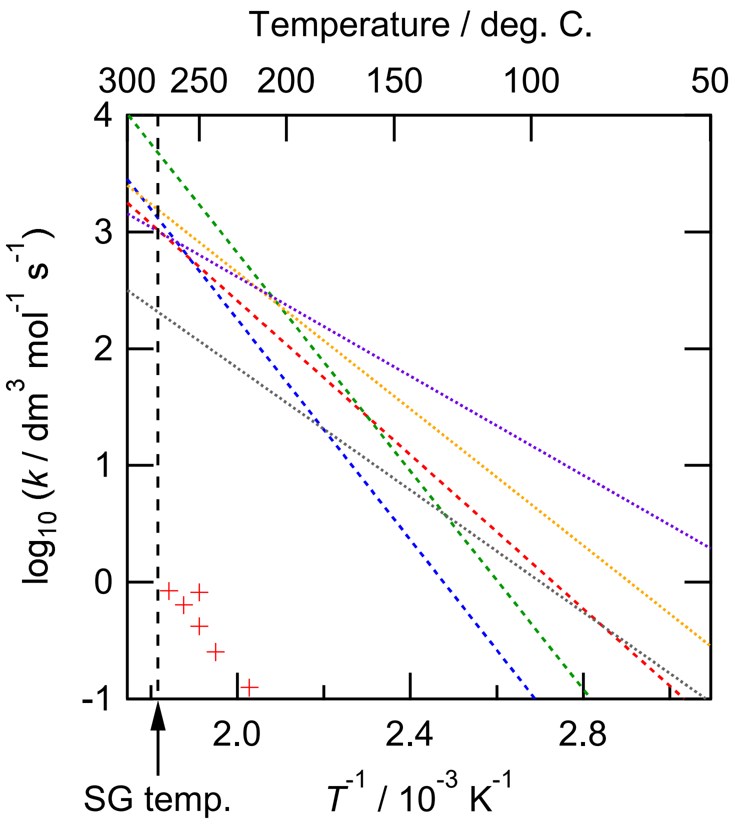
Example of corrosion potential evaluation

- Corrosion potential was stabilized at similar levels with the addition of either hydrazine or carbohydrazide
  - No potential drop observed after addition of carbohydrazide
- Measurements for other candidate substances are now in progress



Another candidate: Ethanolamine (ETA)

- Worldwide common pH controlling agent
- Also has oxygen scavenging ability (slightly)
  - Much slower, but higher concentration in actual plant
  - Possibly ETA stand-alone water chemistry could be an option



The evaluation of reaction rate for ETA was conducted in collaboration with EDF/MAI.

Summary

- Need to prepare alternatives before hydrazine is unavailable
- Literature review to find hydrazine alternative candidates
- Basic studies to obtain data not available in the literature review
  - Evaluation of reaction rates with same equipment
  - Quantitative analysis of carboxylic acid production
  - Measurement of corrosion potential at SG temperature (in progress)

Foreseen transition of oxygen scavenger in PWR secondary system currently

Present	Near future	Future
Hydrazine	Carbohydrazide	N,N-Diethylhydroxylamine?