JAEA

Improved Sampling Technique

IAPWS International Collaboration

Analysis of ion and crud deposition along the sampling

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Background and Objectives

Background

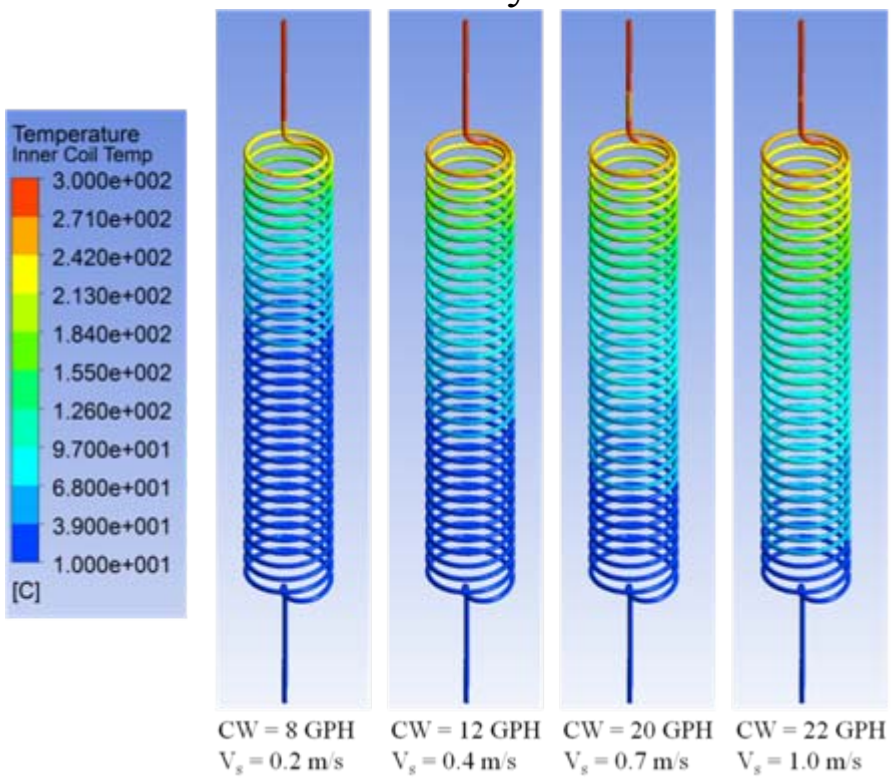
- "hold-up" of iron-base corrosion products in the sampling line and cooler of an autoclave system has been measured in the UNB.
- Temperature distribution along the sampling line and cooler has also calculated precisely by a CFD code.
- Iron concentration measured in the sampled water was strongly affected by solubility of ferrous ion along the sampling line.
- However, in some case (neutral at 150C in the autoclave), measured one was much lower than the expected value from the solubility analysis.

Objectives

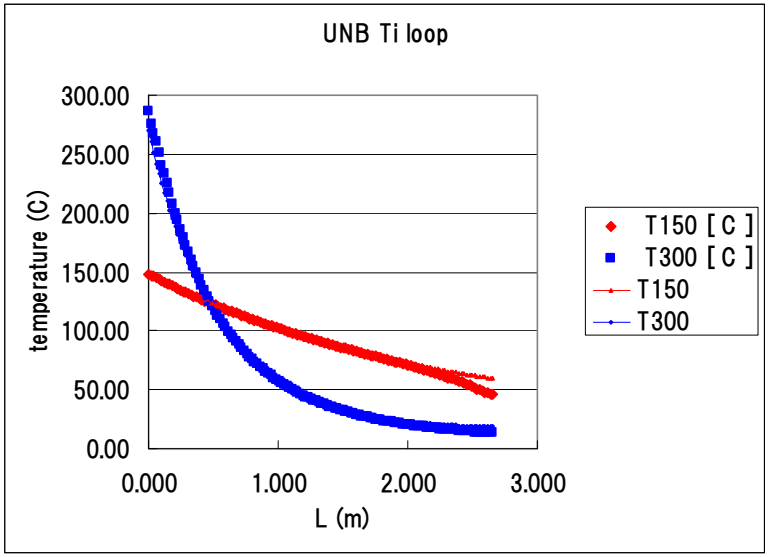
- A numerical simulation model for formation of oxide particle due to super saturation of ferrous ion, deposition and release of particles and ion on sampling line is proposed.
- The experimental results shown above is traced by the model.
- The phenomena of ferrous ion along the sampling line is going to understand for improving the sampling technique

Understanding temperature distribution

Calculated by a CFD code



Temperature profile obtained from best fitting of the CFD results



Temperature was determined by autoclave temperature, sampling and cooling flow rates

Summary of measured results

Autoclave temperature	pH (-)	[Fe] $_{\text{sampled water}}$	solubility (ppb)
300°C	$pH_{25°C}$ 7	4.0 ± 1.0 ppb	$sol_{300°C}$: 5 ppb $sol_{15°C}$: ~60*ppb
300°C	$pH_{25°C}$ 10 (LiOH)	0.28 ± 0.31 ppb	$sol_{300°C}$: 1.1 ppb $sol_{15°C}$: ~0.1*ppb
150°C	$pH_{25°C}$ 7	1.6 ± 2.6 ppb $[Fe]_{\text{cooled autoclave}}$ 0.22 ± 0.09 ppb. $[Fe]_{\text{depositing on sampling line (hotlef)}}$ 41.6 ppb (18.6 µg for 446.5 mL) $[Fe]_{\text{(hotleg)}}$ 10.5 µg $[Fe]_{\text{(coldleg)}}$ 8.1 µg	$sol_{150°C}$: 112 ppb $sol_{15°C}$: ~60*ppb

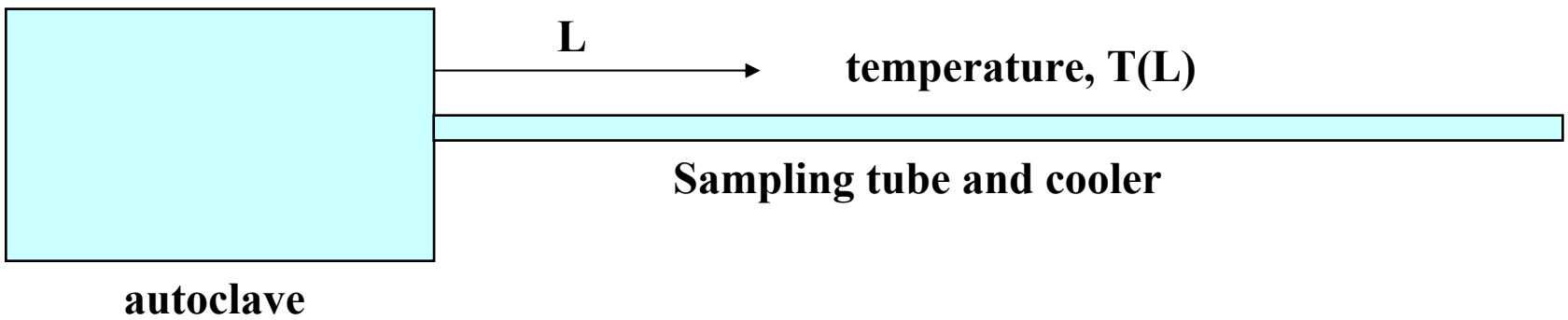
N.B. $sol_{150°C}$ - *$sol_{15°C}$ = ~52 ppb.

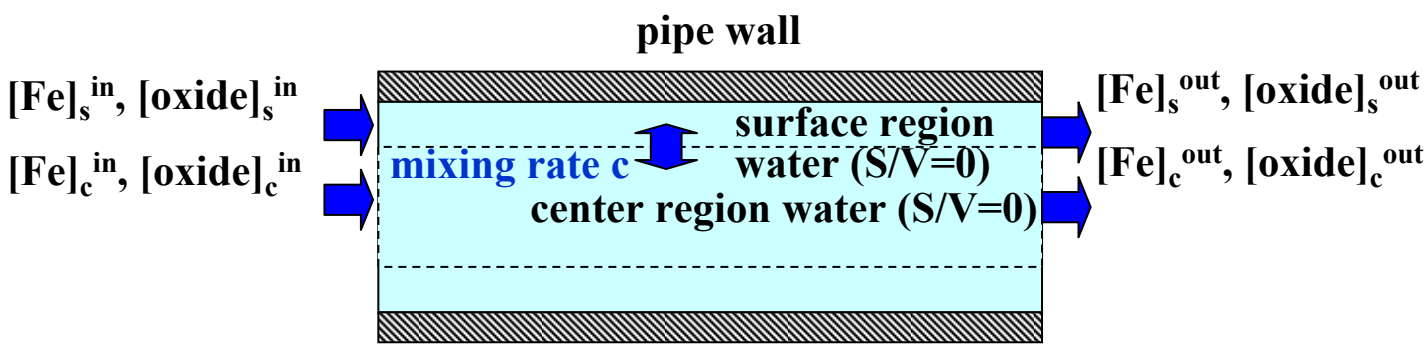
* *extrapolation*

Model assumption

Mixing model of ferrous ion and oxide particles in the water along the flow path

temperature, T





1) super saturated ferrous ion => oxide particles
2) Oxide particles deposit on the surface
3) Deposited oxide particles release into water
4) Deposited oxide particles dissolve into water

Basic equations of the model

Transfer of Fe^{2+} along the surface:

$$dC^s_{Fe}(z,t)/dt\ u = -\chi S^c/V^s C^s_{Fe}(z,t) + \chi^* S^c/V^s C^c_{Fe}(z,t) - k_g C^s_{Fe}(z,t) f_b(C^s_{Fe})$$

cross flow — particulate out

$$-\delta^*_{Fe} C^s_{Fe}(z,t)\ S^s/V^s \quad -\delta^{**}_{Fe} C^s_{Fe}{}^3(z,t)\ S^s/V^s \quad +\zeta_{Fe} T_{Fe}(z,t) S^s/V^s \qquad (1)$$

adsorption — deposition as magnetite — dissolution

$$dC^s_o(z,t)/dt\ u =$$

$$-\chi S^c/V^s C^s_o(z,t) + \chi^* S^c/V^s C^c_o(z,t) + k_g C^s_{Fe}(z,t) f_b(C^s_{Fe})/W_o - k_d C^s_o(z,t) S^s/V^s + \zeta_o T_o(z,t)/W_o S^s/V^s \qquad (2)$$

cross flow — particulate in — deposition — release

Transfer of Fe^{2+} along the center:

$$dC^c_{Fe}(z,t)/dt\ u = -\chi S^c/V^c C^c_{Fe}(z,t) + \chi^* S^c/V^c C^s_{Fe}(z,t) - k_g C^c_{Fe}(z,t) f_b(C^c_{Fe}(z,t)) \qquad (3)$$

cross flow — particulate out

$$dC^c_o(z,t)/dt\ u = -\chi^* S^c/V^c C^c_o(z,t) + \chi S^c/V^c C^s_o(z,t) + k_g C^c_{Fe}(z,t) f_b(C^c_{Fe}(z,t))/W_o \qquad (4)$$

cross flow — particulate in

Formation of oxide film:

$$dT_{Fe}(z,\tau)/dt = +\delta^*_{Fe} C^s_{Fe}(z,\tau) \quad +\delta^{**}_{Fe} C^s_{Fe}{}^3(z,t)\ S^s/V^s \quad -\zeta_{Fe} T_{Fe}(z,\tau) \qquad (5)$$

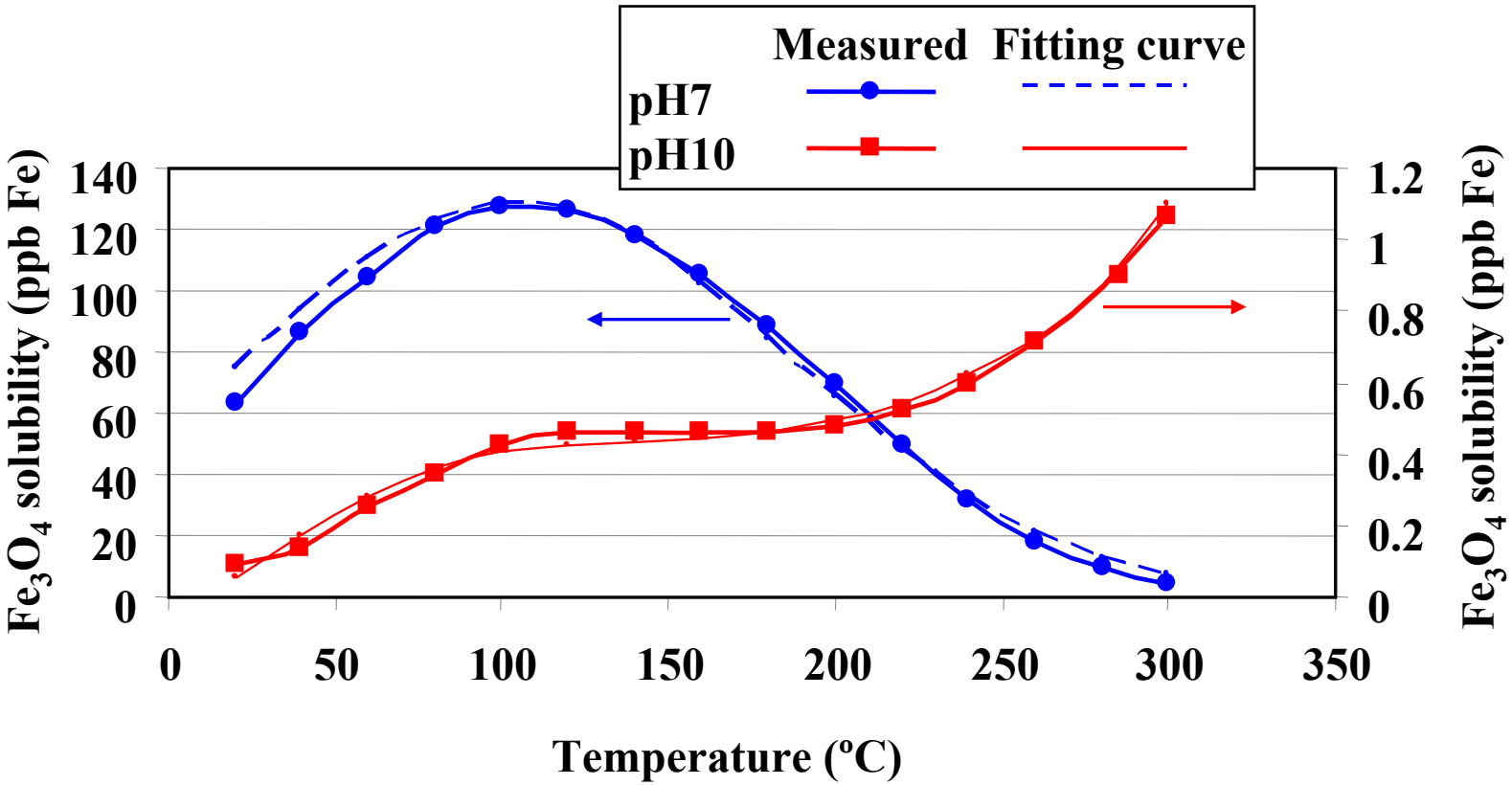
deposition — deposition as magnetite — dissolution

$$dT_o(z,\tau)/dt = +k_d C^s_o(z,\tau) W_o \quad -\zeta_o T_o(z,\tau) \qquad (6)$$

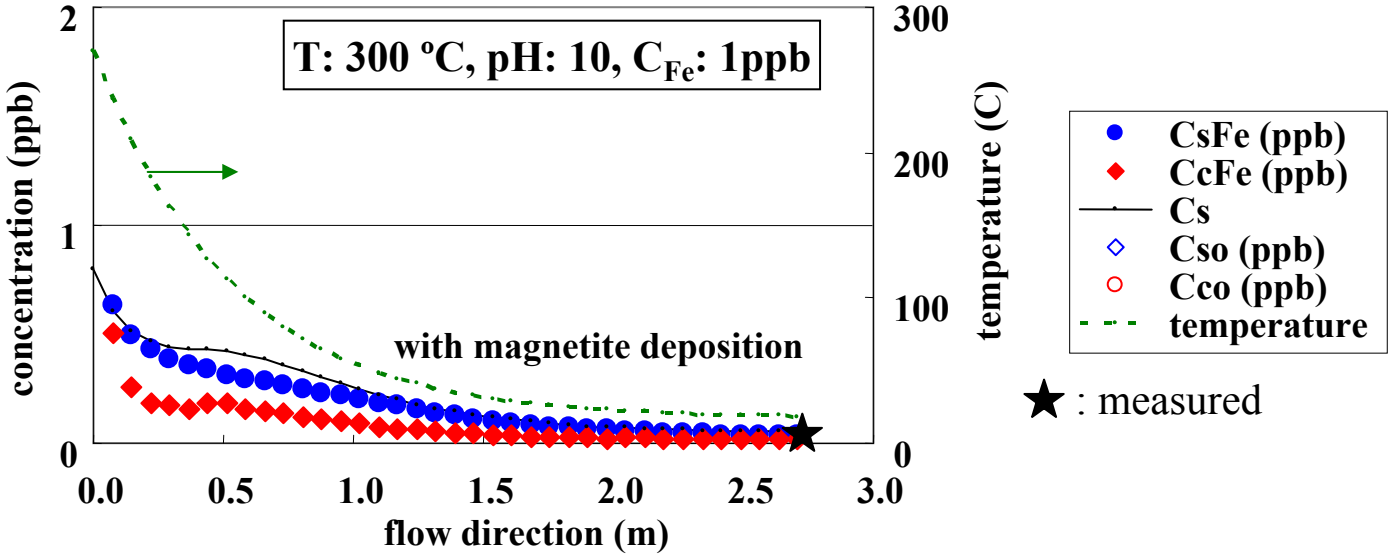
deposition and adsorption — dissolve and release

Newly applied term

Solubility

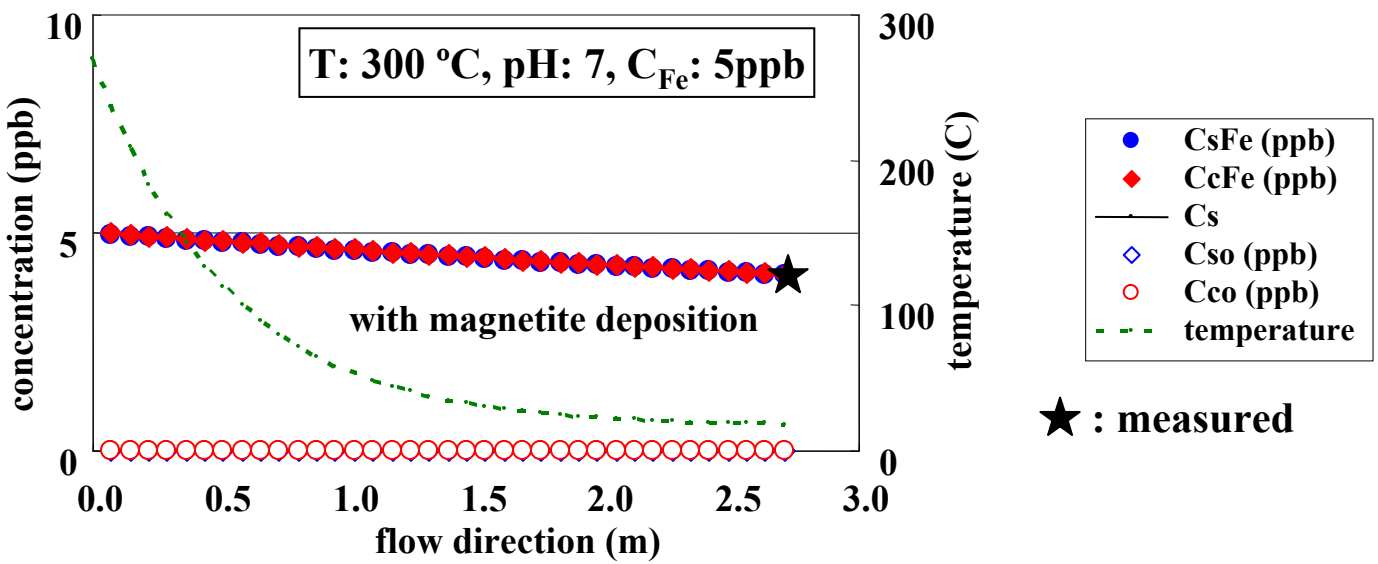

Measured
Fitting curve
pH7
pH10
Fe_3O_4 solubility (ppb Fe)
140
120
100
80
60
40
20
0
1.2
1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
250
300
350
Temperature (ºC)

Calculated results (2)



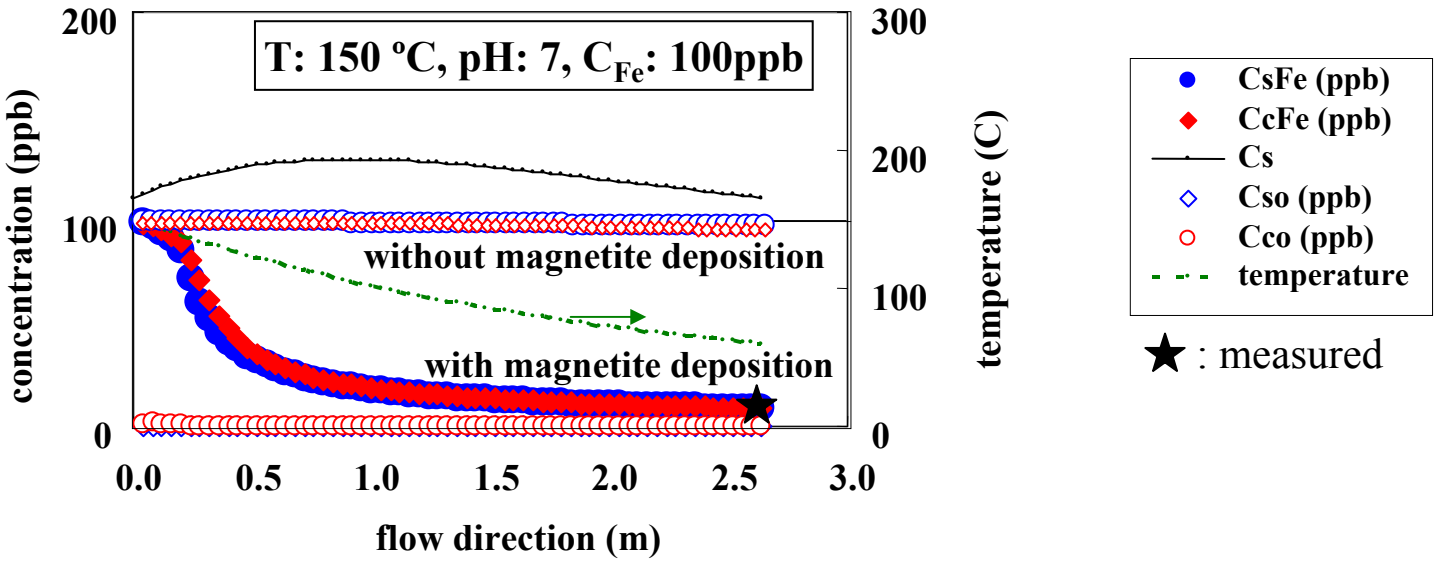
■ Fe concentration decreased as solubility along the sampling line.

Calculated results (1)



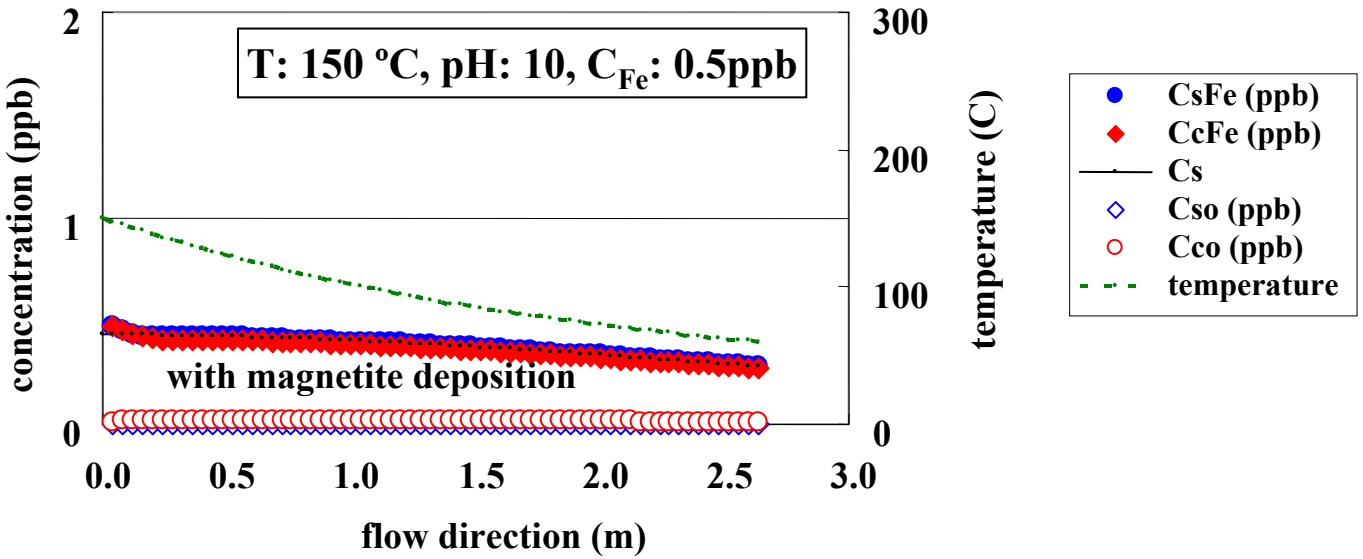
■ Fe concentration at the sampling line inlet might be determined by solubility.

Calculated results (3)



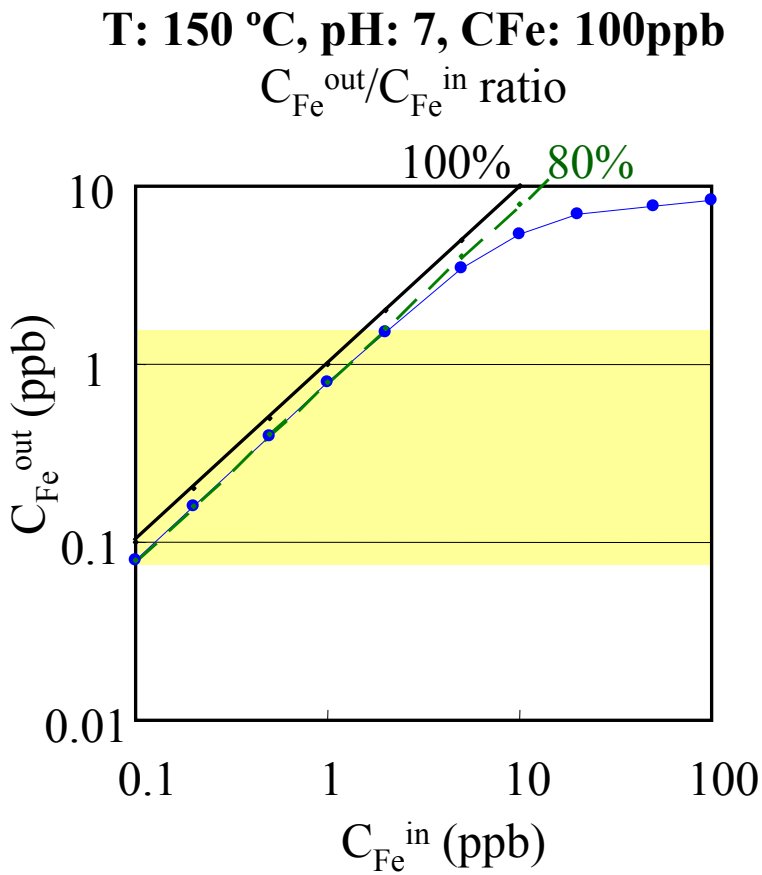
- Spinel deposition might result in contamination of sampling line.
- Spinel deposition might be observed at the autoclave inner surface, which resulted in depression of Fe concentration in the autoclave.

Calculated results (4)



■ Fe concentration decreased as solubility along the sampling line.

Calculated results (5)



Determination range should be carefully evaluated

Discussions

① In the model, it was considered that ferrous ion precipitated as particles on the water due to super saturation and some of them deposited on the surface.

② Direct formation of magnetite on the surface was also considered.

③ Fe concentration decreased as solubility along the sampling line due to ①.
(300ºC,150ºC, pH10)

④ Fe concentration decreased as solubility along the sampling line due to ①.
(300ºC, pH7)

⑤ When Fe concentration in the autoclave was high enough, that decreased much lower than solubility due to ①. (150ºC, pH7)

⑥ Magnetite deposition might result in contamination of sampling line due to ②.
(150ºC, pH7)

⑦ Magnetite deposition might be observed at the autoclave inner surface, which resulted in depression of Fe concentration in the autoclave. (150ºC, pH7)

⑧ Determination range should be carefully evaluated for precise analysis

Recommendation on the sampling technique

① In order to validate the measured concentration in the sampled water, the distributions of temperature and solubility along the sampling line from the main line to the sampling line outlet is essential

② Validation of the measured concentration based on the solubility analysis is required.

③ Even when the measure concentration is lower than the solubility through sampling line, loss of magnetite formation along the sampling line should be carefully evaluated.

Summary

· A ferrous ion deposition and release model was proposed.

· The measured results of the sampling line experiment were well analyzed with the model.

· Application of the model might be a hopeful tool for validation of the sampling data at the plants.
· The model should be extended to apply different pH, temperature and flow velocity for plant application.
· Major calculation constants should be carefully re-evaluated for application.