Enhanced removal of sodium salts supported by *in-situ* catalyst synthesis in a supercritical water oxidation process

F. Takahashi, Z. R. Sun, K. Fukushi, Y. Oshima and K. Yamamoto

ABSTRACT

For practical applications of supercritical water oxidation to wastewater treatment, the deposition of inorganic salts in supercritical phase must be controlled to prevent a reactor from clogging. This study investigated enhanced removal of sodium salts with titanium particles, serving as a salt trapper and a catalyst precursor, and sodium recovery by sub-critical water. When Na_2CO_3 was tested as a model salt, sodium removal efficiency was higher than theoretically maximum efficiency defined by Na_2CO_3 solubility. The enhanced sodium removal resulted from *in-situ* synthesis of sodium titanate, which could catalyse acetic acid oxidation. The kinetics of sodium removal was described well by a diffusion mass-transfer model combined with a power law-type rate model of sodium titanate synthesis. Titanium particles showed positive effect on sodium removal in the case of NaOH, Na_2SO_4 and Na_3PO_4. However, they had negligible effect for NaCl and negative effect for Na_2CrO_4, respectively. More than 99% of trapped sodium was recovered by sub-critical water except for Na_2CrO_4. In contrast, sodium recovery efficiency remained less than 50% in the case of Na_2CrO_4. Reused titanium particles showed the same performance for enhanced sodium removal. Enhanced salt removal supported by *in-situ* catalyst synthesis has great potential to enable both salt removal control and catalytic oxidation.

Key words | kinetics, salt deposition control, sodium removal, sodium titanate synthesis, supercritical water oxidation

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INTRODUCTION

The oxidation in supercritical water (SCWO) has attracted a great deal of attention as an innovative process of hazardous organic compounds treatment (Thomason & Modell 1984; Modell 1989; Barner *et al.* 1992; Gloyna & Li 1993). Water above its critical point (374 °C, 22.1 MPa), called supercritical water, can serve as an excellent reaction medium for rapid and complete oxidation of hazardous organic compounds without interphase mass-transfer limitations. For practical applications of SCWO to wastewater treatment, however, two problems must be overcome.

The first problem is severe corrosion of a reactor due to high temperature operation. To enable lower temperature operation with sufficient oxidation efficiency, catalysed SCWO of refractory organic compounds has been investigated (Krajnc & Levec 1994; Ding *et al.* 1996; Oshima *et al.* 1999; Savage *et al.* 2006). Takahashi *et al.* (2012) reported that sodium titanate, which was hydrothermally

synthesized on the surface of titanium particles in supercritical water, had catalytic activity on SCWO of acetic acid. The other problem is fatal plugging at bottlenecks of SCWO zone. Inorganic salts contained in wastewater would precipitate there due to extremely low solubility in supercritical water (Armellini & Tester 1991, 1993; Cui & Harris 1995). It is important to control inevitable salt deposition in supercritical phase when sufficient pre-removal of inorganic salts in wastewater is difficult due to cost and/or technical reasons. Hodes *et al.* (2004) reviewed fundamental physicochemical characteristics of salt precipitation and Marrone *et al.* (2004) summarized some commercial approaches to salt precipitation control. A reverse flow tank reactor with two distinct thermal zones, which was suggested by Barner *et al.* (1992) and Hong *et al.* (1989), is an approach for salt control. Inorganic salts precipitated in upper supercritical zone, dropped to lower sub-critical

zone and were removed from a reactor. Daman (1996, 1998) and Fauvel et al. (2004) suggested a double-wall reactor, in which a supercritical water radial flow dilutes corrosive species near reactor wall and prevents sticky solids from depositing on the wall. Reversible flow tubular reactor, suggested by Whiting (1996, 1997), enabled the removal of precipitated salts by periodically reversed water supply under sub-critical conditions.

This study focuses on titanium particles which were used for *in-situ* synthesis of sodium titanate catalyst (Takahashi *et al.* 2012). Titanium particles might enable both salt deposition control and catalytic SCWO at the same time. Because titanium particles increase contact surface area, they will promote salt precipitation until salt concentration in the bulk decreases to solubility. This means that inorganic salts will hardly be deposited in downstream part after enough salt removal. Therefore, supercritical phase can be separated into salt removal part and following non-precipitation part. A proposed process is illustrated in Figure 1(a). If salt removal can be simulated kinetically, it is possible to expect available SCWO treatment time until the plugging at salt removal zone. Before the plugging, sub-critical water will be fed into a reactor to recover precipitated salts from salt deposition zone. Unlike supercritical water, sub-critical water can dissolve inorganic salts. Operational switch from SCWO treatment to salt recovery is possible by only decreasing temperature.

The objective of this study is to investigate three topics. The first is enhanced removal of various sodium salts with titanium particles. The kinetics of sodium removal was investigated when Na_2CO_3 was tested as a model salt. The second is sodium recovery by sub-critical water. The last is

to investigate the performance of reused titanium particles for enhanced sodium removal.

MATERIALS AND METHODS

Surface area of titanium particles

Particles of sponge titanium (Toho titanium Inc., Japan, and Sumitomo titanium Inc., Japan, purity > 98%, diameter: 0.84–3.35 mm) were used in sodium removal experiments. Surface area of titanium particles was measured by BET method using a surface analyser (TriStar-3000: Micrometrics Inc., USA). Krypton gas was used as adsorbate.

Experimental apparatus

Experimental apparatus consisted of high-pressure pumps, pre-heating lines, a reactor, a type-K thermocouple, a heat exchanger, a backpressure regulator, and a gas–liquid separator. An isothermal, isobaric plug flow reactor fabricated from SUS 316 tube (7.05 mm inner diameter, 7 cm length, 2.73 mL internal volume) was used in all experiments. They are illustrated in Figure 1(b) and detailed apparatus was described by Takahashi *et al.* (2012). Titanium particles were placed in the reactor with filling density of 354.5–1,115 g/L or were not placed. Pure water was degassed by nitrogen gas before use. Solution of a reagent like Na_2CO_3 and pure water were fed separately into the reactor at 25 MPa and heated to targeted temperature (350 or 450 °C) in pre-heating line. Fed solutions were mixed before the reactor and passed through it at the residence
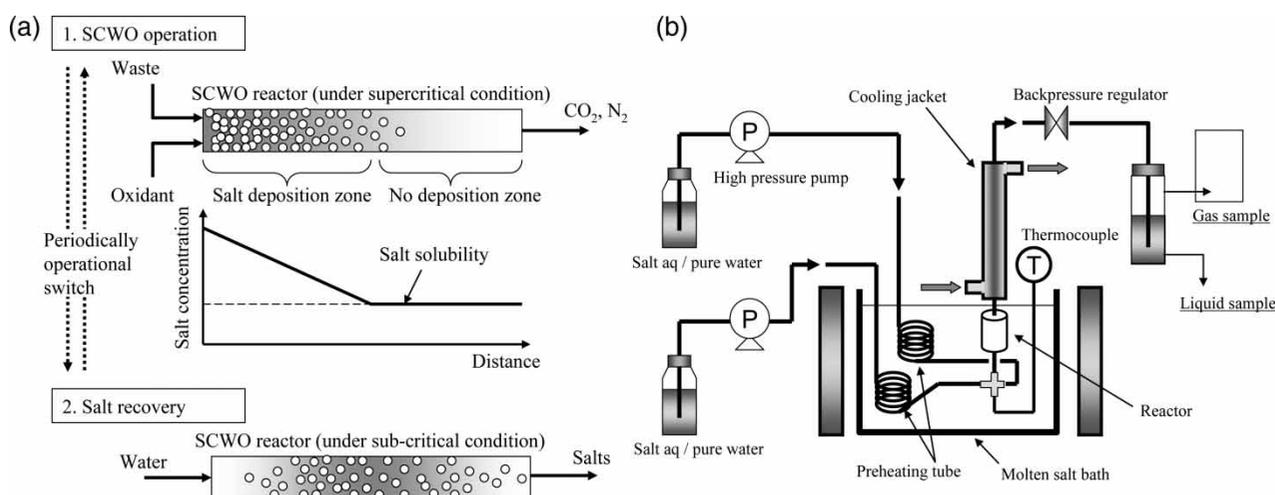

Figure 1 | A proposed process for salt control using titanium particles by periodically operational condition switch (a) and experimental apparatus (b).

time of 1.7–9.7 s. Residence times were calculated by dividing bulk volume of a reactor by volumetric feed rate under supercritical conditions. The bulk volume of a reactor was obtained by subtracting catalyst volume from volume of the reactor. After the effluent were cooled and depressurized, liquid and gas samples were collected at the sampling port using a glass container and a gas bag, respectively.

Sodium removal experiment

All sodium salts (NaCl, NaOH, Na_2CO_3, Na_2SO_4, Na_3PO_4, and Na_2CrO_4) utilized in this paper were analytical grade (Wako Inc., Japan, purity of each reagent: >99%). The operational conditions of sodium removal experiments are listed in Table 1. Sodium concentration in the effluent was measured by ion chromatography (IC-500: Shimadzu Inc., Japan). When Na_2CrO_4 was tested, chromium concentration in the effluent was also measured by inductively-coupled plasma mass spectrometry (HP4500: Yokogawa Analytical Systems Inc., Japan). Fresh titanium particles were always used in all sodium removal experiments. Only when the performance of reused titanium particles on sodium removal was investigated, however, reused titanium particles were used instead of fresh ones. After sodium removal experiment, the reactor was depressurized and cooled. And then, 350 mL of pure water was fed into the reactor for surface cleaning under ambient conditions. Titanium particles were sampled to confirm hydrothermal synthesis of sodium titanate during sodium removal experiments. The surface of titanium

particles was observed by scanning electron microscope (SEM; JXA-8200: JEOL Inc., Japan) and elemental composition of synthesized minerals on titanium particles was analysed by scanning electron microscope-electron probe microanalyser (SEM-EPMA; JXA-8200: JEOL Inc., Japan). When the surface of titanium particles was not observed, sodium recovery experiments were conducted sequentially after sodium removal experiments.

Sodium recovery experiment

After sodium removal experiment, temperature of molten salt bath decreased to 350 °C without a feed of pure water/ salt solution. When the temperature reached 350 °C, pure water was fed to the reactor at 25 MPa (sub-critical conditions). The volume of supplied pure water was 150 mL increased to 250 mL if necessary. Sodium concentration in the effluent was measured by ion chromatography. The amount of recovered sodium was compared with total deposited/incorporated sodium on titanium particles to confirm recovery efficiency under sub-critical conditions.

RESULTS AND DISCUSSION

The effect of titanium particles on sodium removal

Sodium concentrations in the effluent with/without titanium particles were compared with identify the effect of titanium particles on sodium removal. The ratio of sodium

Table 1 | Operating conditions of sodium removal and sodium recovery experiments

Salt (–)	Concentration range (in supercritical phase) (mol-Na/L)	Residence time in a reactor (s)	Sampling time from experiment start (time on-stream) (min)	Filling density (g/L)	Specific surface area per unit bulk volume (mm^{-1})
Na_2CO_3	9.54×10^{-5}–4.77×10^{-4}	1.7–9.7	70, 130, 190, 250, 310	0	0.7485
Na_2CO_3	1.91×10^{-4}	9.0 ± 0.1	70, 130, 190, 250, 310	354.5	5.104
Na_2CO_3	1.91×10^{-4}	8.1 ± 0.1	70, 130, 190, 250, 310	790.9	14.59
Na_2CO_3	9.54×10^{-5}–4.77×10^{-4}	7.6 ± 0.1	70, 130, 190, 250, 310	973.9	30.06
Na_2CO_3	1.91×10^{-4}	7.2 ± 0.07	70, 130, 190, 250, 310	1,115	38.88
NaCl	1.91×10^{-4}	7.2 ± 0.1	70, 130, 190, 250, 310	1,115	38.88
NaOH	1.91×10^{-4}	7.2 ± 0.1	70, 130, 190, 250, 310	1,115	38.88
Na_2SO_4	1.91×10^{-4}	7.2 ± 0.1	70, 130, 190, 250, 310	1,115	38.88
Na_3PO_4	1.91×10^{-4}	7.2 ± 0.1	70, 130, 190, 250, 310	1,115	38.88
Na_2CrO_4	1.91×10^{-4}	7.2 ± 0.1	70, 130, 190, 250, 310	1,115	38.88
–	–	7.2 ± 0.1	50, 70	1,115	38.88

*All runs of sodium removal experiments and sodium recovery experiments were operated at 25 MPa, 450 °C (supercritical conditions) and 25 MPa, 350 °C (sub-critical conditions), respectively.

concentration with titanium particles to that without titanium particles is shown in Figure 2.

If the ratio is less than 1.0, it means promotional effect on sodium removal. When NaCl and Na_2CrO_4 were tested, titanium particles showed negligible and negative effect, respectively. Negligible effect on sodium removal resulted from high solubility of NaCl (3.79×10^{-3} mol-Na/L at 25 MPa and 450 °C, referred from Armellini & Tester 1993). When initial concentration of NaCl increased five times higher (4.77×10^{-4} mol-Na/L at 25 MPa, 450 °C), sodium removal efficiency in the presence of titanium particles was less than 0.04, according to lower initial concentration than the solubility. On the other hand, negative effect on sodium removal in the case of Na_2CrO_4 needs further study for mechanism-based explanation. This finding might result from partial hydrolysis of Na_2CrO_4 to NaOH and H_2CrO_4, which would be converted to Cr_2O_3 due to high temperature. If the solubility of NaOH in supercritical water is higher than that of Na_2CrO_4, partial hydrolysis to NaOH will contribute to less sodium removal. Positive effect of titanium particles on chromium removal seems to result from lower solubility of Cr_2O_3 than that of Na_2CrO_4. This result cannot be supported by any reference due to no solubility data in supercritical water. However, it is noted that Cr_2O_3 solubility under ambient conditions (20 °C) is greatly lower than that of Na_2CrO_4. They are less than 1.00×10^{-3} mol/L for Cr_2O_3 and 3.27 mol/L for Na_2CrO_4, respectively. When NaOH and Na_2CO_3 were tested, greatly positive effect on sodium removal appeared.
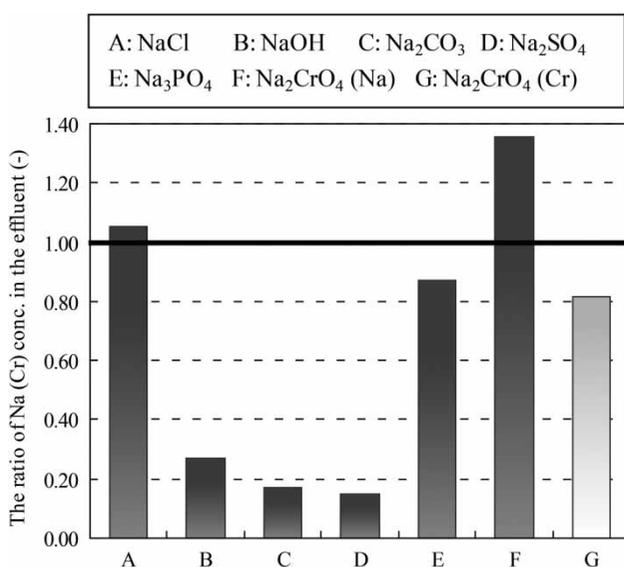
This resulted from not only accelerated deposition of sodium salts but also hydrothermal synthesis of sodium titanate. The formation of sodium titanate on titanium particle surface consumed sodium in the bulk and resulted in higher sodium removal efficiency. Strongly positive effect on sodium removal in the case of Na_2SO_4 might be explained by only accelerated deposition of Na_2SO_4. Obvious synthesis of sodium titanate was not confirmed by SEM observation. These results in summary show that titanium particles could promote sodium removal through accelerated deposition and hydrothermal synthesis of sodium titanate. However, negative effect should be concerned in the case of complex metal oxides like Na_2CrO_4.

The impact of sodium titanate synthesis on sodium removal

Sodium removal efficiency has theoretical maximum value when sodium concentration in the effluent is equal to the solubility of a salt. For example, maximum sodium removal efficiency in the case of Na_2CO_3 at 25 MPa, 450 °C, and 9.54×10^{-5} mol-Na/L of initial concentration (in supercritical phase) was calculated to be 0.245. The solubility of Na_2CO_3 at 25 MPa and 450 °C (7.21×10^{-5} mol-Na/L) was referred from Khan & Rogak (2004) in this calculation. Figure 3(a) shows sodium removal efficiency as a function of specific surface area per unit bulk volume at 25 MPa, 450 °C, and 9.54×10^{-5} mol-Na/L of Na_2CO_3 initial concentration. All data at different on-stream sampling times are plotted in Figure 3(a). When specific surface area was more than 14.59 mm^{-1}, sodium removal efficiency was always higher than the theoretical maximum (0.245). This finding means that sodium concentration in the effluent decreased less than Na_2CO_3 solubility. Hydrothermal synthesis of sodium titanate on the surface of titanium particles, shown in Figure 3(b), resulted in excess lower sodium concentration than the solubility. From the viewpoint of salt deposition control, enhanced sodium removal supported by sodium titanate synthesis is desirable to prevent sodium deposition in downstream part. Sodium removal efficiency gradually decreased at any specific surface area with increasing on-stream sampling time. This result means that formation rate of sodium titanate decreased steadily with on-stream sampling time. The results shown in Figure 3(a) suggest that sodium titanate synthesis needs to be considered in the kinetics of sodium removal.
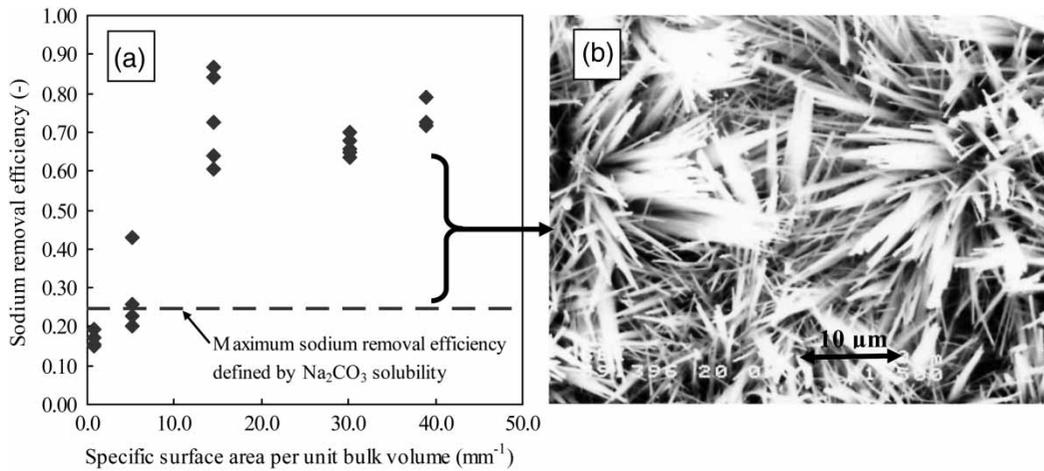

Figure 2 | Comparison of sodium concentration in the effluent with/without titanium particles.

Figure 3 | Sodium removal efficiency as a function of specific surface area per unit bulk volume (a) and SEM photograph of synthesized sodium titanate (b).

Kinetics of sodium removal (Na$_2$CO$_3$ case)

When initial fed Na$_2$CO$_3$ concentration was higher than the solubility, Na$_2$CO$_3$ would be nucleated in the bulk phase and then precipitated in a reactor. In this case, kinetics of nucleated Na$_2$CO$_3$ behaviour, which was sodium removal from the bulk phase, should take two sodium mass-transfers into account. The first is mass-transfer from the bulk (supercritical water) to the wall surface of a reactor. The other is the transfer from the bulk to the surface of titanium particles. Driving force of these transfers is the diffusion due to concentration difference between the bulk and the surface. Therefore, the transfers to the reactor wall or to the surface of titanium particles are expressed in following forms (Equations (1), (2)), respectively.

$$r_{Dep-Wall} = k_{Wall} * S_{Wall} * (C - C_{S,Wall}) \qquad (1)$$

$$r_{Dep-TP} = k_{TP} * S_{TP} * (C - C_S) \qquad (2)$$

where $r_{Dep-Wall}$, k_{Wall}, S_{Wall}, C, and $C_{S,Wall}$ in Equation (1) mean rate of sodium mass-transfer to the reactor wall, coefficient of sodium mass-transfer to the reactor wall, surface area of the reactor wall, sodium concentration in the bulk, and sodium concentration near the surface of reactor wall, respectively. r_{Dep-TP}, k_{TP}, S_{TP}, and C_S in Equation (2) mean rate of sodium mass-transfer to the surface of titanium particles, coefficient of sodium mass-transfer to the surface of titanium particles, and sodium concentration near the surface of titanium particles, respectively. On the surface of the reactor wall, phase equilibrium between deposited and dissolved Na$_2$CO$_3$ was assumed. Therefore, sodium concentration near the surface of the reactor wall ($C_{S,Wall}$) was defined to be equal to Na$_2$CO$_3$ solubility (C_{Sat}). In contrast, phase equilibrium could not be assumed near the surface of titanium particles because some of the sodium near titanium particle surface would be used for sodium titanate synthesis. Synthesis rate of sodium titanate should depend on sodium concentration near the surface (C_S) and surface area of titanium particles (S_{TP}). In this study, linear proportion of sodium concentration near the surface (C_S) and surface area of titanium particles (S_{TP}) to the synthesis rate was assumed. The synthesis rate (r_{Syn}) can be expressed in following form (Equation (3)).

$$r_{Syn} = k * S_{TP} * C_S \qquad (3)$$

where k is rate constant of sodium titanate synthesis. Considering material balance of sodium in the bulk, disappearance rate of sodium in the bulk ($-dC/dt$) is equal to the sum of transferred sodium to reactor wall and titanium particles ($r_{Dep-Wall}$, r_{Dep-TP}).

$$- dC/dt = r_{Dep-Wall} + r_{Dep-TP} \qquad (4)$$

Equation (4) can be expressed by following equation (Equation (5)) using Equations (2), (3) and the equality between $C_{S,Wall}$ and C_{Sat}.

$$-dC/dt = k_{Wall} * S_{Wall} * (C - C_{S,Wall}) + k_{TP} * S_{TP} * (C - C_S) \qquad (5)$$

Considering material balance of sodium near the surface of titanium particles, following equation is introduced

(Equation (6)).

$$- dC_S/dt = k * S_{TP} * C_S - k_{TP} * S_{TP} * (C - C_S) \qquad (6)$$

Although surface area of titanium particles (S_{TP}) would increase with on-stream sampling time due to sodium titanate synthesis, S_{TP} is approximated to be constant and equal to initial surface area. Three parameters of Equations (5) and (6), which were coefficient of sodium mass-transfer to the reactor wall (k_{Wall}), coefficient of sodium mass-transfer to titanium particle surface (k_{TP}), and rate constant of sodium titanate synthesis (k), were optimized by non-linear regression to fit experimental results. Parity plots of model-predicted vs measured sodium removal efficiency and of model-predicted vs measured sodium concentration in the effluent, are shown in Figure 4. The diffusion mass-transfer model combined with the power law-type rate model of sodium titanate synthesis could express experimental results well. Further study under wide-range conditions and with other inorganic salts is necessary to verify this combined model applicability to the simulation of salt removal by titanium particles.

Sodium recovery by sub-critical water

Sodium deposited on titanium particles and incorporated into sodium titanate was recovered from a reactor by sub-critical water (25 MPa, 350 °C). Sodium recovery efficiencies were 0.87 for NaCl, 0.89 for NaOH, 0.91 for Na_2CO_3, 0.96 for Na_2SO_4, 0.99 for Na_3PO_4, and 0.31 for Na_2CrO_4, respectively. Although sodium recovery efficiency in the case of NaCl likely includes large uncertainty due to small amount of deposited sodium, most deposited sodium (NaCl) seems to be recovered. Approximately 100% recovery of deposited sodium was confirmed in the case of Na_3PO_4. On the other hand, incomplete recovery of deposited sodium was measured in the case of NaOH, Na_2CO_3, Na_2SO_4, and, in particular, Na_2CrO_4. Except for Na_2CrO_4, 4.3–9.6% of deposited sodium still remained on titanium particles even after sub-critical water cleaning. Residual sodium likely resulted from undecomposed sodium titanate in the case of NaOH and Na_2CO_3 and was undissolved Na_2SO_4 in the case of Na_2SO_4. Additional 100 mL of sub-critical water feed could achieve approximately 99% of sodium recovery ratio. On the other hand, sodium recovery efficiency in the case of Na_2CrO_4 was greatly lower than for other sodium salts (30.6%). This figure still remained less than 50% after additional sub-critical water cleaning. Low hydrolysis rates of Cr-Na-Ti complex mineral under sub-critical conditions likely cause lower sodium recovery efficiency. Although sub-critical water is effective for sodium recovery, further study is necessary to promote the decomposition of metal complex minerals under sub-critical conditions for sufficient sodium recovery from any sodium salt.
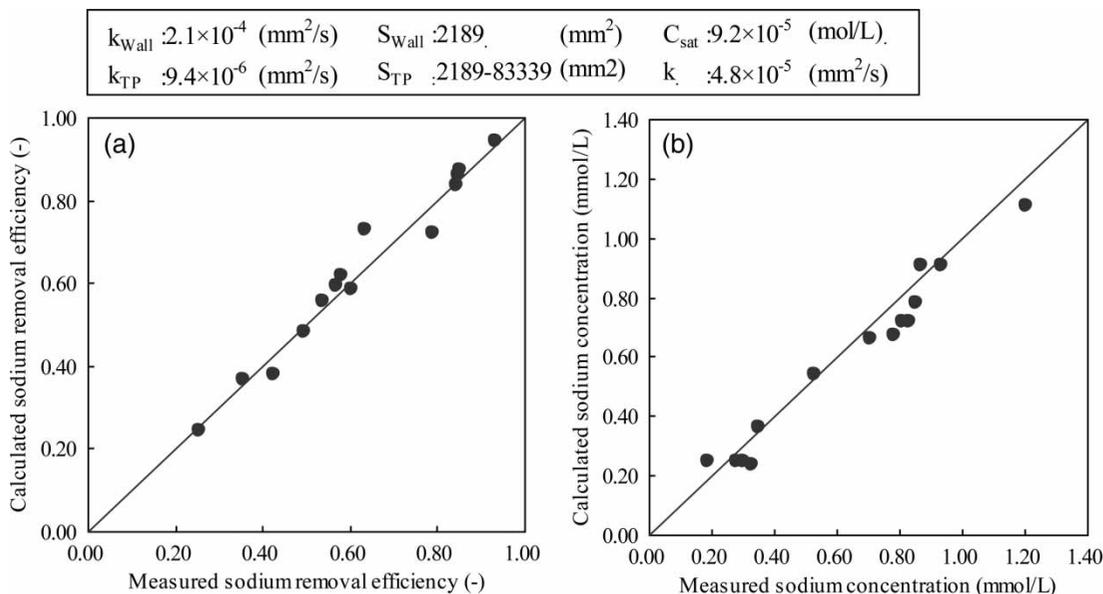

| k_{Wall} :2.1×10^{-4} (mm²/s) | S_{Wall} :2189 (mm²) | C_{sat} :9.2×10^{-5} (mol/L) |
| k_{TP} :9.4×10^{-6} (mm²/s) | S_{TP} :2189-83339 (mm2) | k :4.8×10^{-5} (mm²/s) |

Figure 4 │ A parity plot of model-predicted vs measured sodium removal efficiency (a) and of model-predicted vs measured sodium concentration in the effluent (b) (25 MPa, 450 °C, initial fed concentration of Na_2CO_3: 9.54×10^{-5}–4.77×10^{-4} mol-Na/L, filling density of titanium particles: 354.5–1,115 g/L).
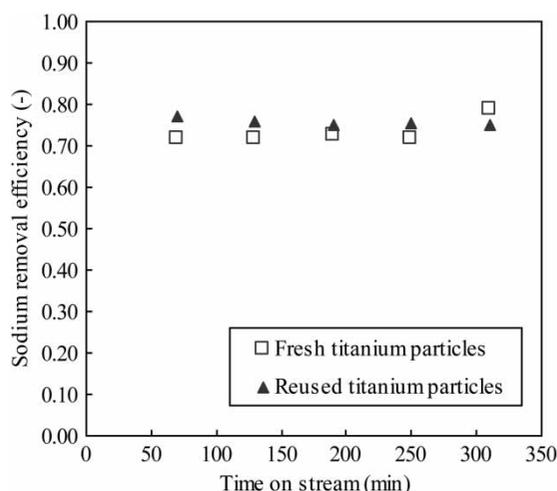
Figure 5 | Sodium removal efficiency with fresh/reused titanium particles.

Sodium removal by reused titanium particles

Titanium particles, which had been used in sodium removal experiment (Na_2CO_3 feed) and sodium recovery experiment, were utilized again in sodium removal experiment under the same condition (Na_2CO_3 feed). Sodium removal efficiency in the presence of fresh/reused titanium particles is shown in Figure 5. Reused titanium particles generated the same removal efficiency as fresh ones. This finding suggested that titanium particles would be continuously available through cyclic operations of sodium removal under supercritical conditions and sodium recovery by sub-critical water. As mentioned in the previous section, however, incomplete recovery of sodium incorporated in metal complex minerals should be overcome for long service time of titanium particles.

CONCLUSION

Enhanced removal of sodium salts with titanium particles, serving as a salt trapper and a catalyst precursor, and sodium recovery by sub-critical water were investigated using a lab-scale small reactor. When Na_2CO_3 was tested, sodium removal efficiency was higher than theoretically maximum efficiency defined by Na_2CO_3 solubility. The enhanced sodium removal resulted from *in-situ* synthesis of sodium titanate. The kinetics of sodium removal was described well by a diffusion mass-transfer model combined with a power law-type rate model of sodium titanate synthesis. Titanium particles showed positive effect on sodium removal in the cases of NaOH, Na_2SO_4 and

Na_3PO_4. On the other hand, they had negligible effect for NaCl and negative effect for Na_2CrO_4, respectively. More than 99% of deposited/incorporated sodium was recovered by sub-critical water except for Na_2CrO_4. However, sodium removal efficiency remained less than 50% in the case of Na_2CrO_4. Reused titanium particles showed the same performance for enhanced sodium removal. Enhanced salt removal supported by *in-situ* catalyst synthesis has great potential to enable salt removal control and catalytic oxidation. A 'desktop-type' small device for on-site waste-water treatment will be one of the expected applications. This study would offer basic and useful information for further development of such SCWO applications. In the industrial-scale applications, however, experiments using a larger reactor are recommended for salt removal kinetic analysis.

REFERENCES

Armellini, F. J. & Tester, J. W. 1991 Experimental methods for studying salt nucleation and growth from supercritical water. *Journal of Supercritical Fluids* **4** (4), 254–264.

Armellini, F. J. & Tester, J. W. 1993 Solubility of sodium chloride and sulfate in sub- and supercritical water vapor from 400–550 °C and 100–250 bar. *Fluid Phase Equilibria* **83**, 123–142.

Barner, H. E., Huang, C. Y., Johnson, T., Jacobs, G., Martch, M. A. & Killilea, W. R. 1992 Supercritical water oxidation: an emerging technology. *Journal of Hazardous Materials* **31** (1), 1–17.

Cui, S. T. & Harris, J. G. 1995 The structure and phase equilibria of salt water solution at supercritical water conditions. *International Journal of Thermophysics* **16** (2), 493–502.

Daman, E. L. 1996 Process and apparatus for supercritical water oxidation, U.S. Patent #5571423.

Daman, E. L. 1998 Process and apparatus for supercritical water oxidation, U.S. Patent #5723045.

Ding, Z. Y., Frisch, M. A., Li, L. X. & Gloyna, E. F. 1996 Catalytic oxidation in supercritical water. *Industrial and Engineering Chemistry Research* **35** (10), 3257–3279.

Fauvel, E., Joussot-Dubien, C., Guichardon, P., Charbit, G., Charbit, F. & Sarrade, S. 2004 A double-wall reactor for hydrothermal oxidation with supercritical water flow across the inner porous tube. *Journal of Supercritical Fluids* **28** (1), 47–56.

Gloyna, E. F. & Li, L. 1993 Supercritical water oxidation: an engineering update. *Waste Management* **13**, 379–394.

Hodes, M., Marrone, P. A., Hong, G. T., Smith, K. A. & Tester, J. W. 2004 Salt precipitation and scale control in supercritical water oxidation – part A: fundamentals and research. *Journal of Supercritical Fluids* **29** (3), 265–288.

Hong, G. T., Killilea, W. R. & Thomason, T. B. 1989 Method for solids separation in a wet oxidation type process, U.S. Patent #4822497.

Khan, M. S. & Rogak, S. N. 2004 Solubility of Na_2SO_4, Na_2CO_3 and their mixture in supercritical water. *Journal of Supercritical Fluids* **30**, 359–373.

Krajnc, M. & Levec, J. 1994 Catalytic-oxidation of toxic organics in supercritical water. *Applied Catalysis B-Environmental* **3** (2–3), 101–107.

Marrone, P. A., Hodes, M., Smith, K. A. & Tester, J. W. 2004 Salt precipitation and scale control in supercritical water oxidation – part B: commercial/full-scale applications. *Journal of Supercritical Fluids* **29** (3), 289–312.

Modell, M. 1989 Supercritical water oxidation. In: *Standard Handbook of Hazardous Waste Treatment and Disposal* (H. M. Freeman, ed.). McGraw-Hill, New York, Section 8.11.

Oshima, Y., Tomita, K. & Koda, S. 1999 Kinetics of the catalytic oxidation of phenol over manganese oxide in supercritical water. *Industrial and Engineering Chemistry Research* **38** (11), 4183–4188.

Savage, P. E., Dunn, J. B. & Yu, J. L. 2006 Recent advances in catalytic oxidation in supercritical water. *Combustion Science and Technology* **178** (1–3), 443–465.

Takahashi, F., Sun, Z. R., Fukushi, K., Oshima, Y. & Yamamoto, K. 2012 Catalytic oxidation of acetic acid over sodium titanate synthesized hydrothermally in supercritical water. *Journal of Supercritical Fluids* **61**, 126–133.

Thomason, T. B. & Modell, M. 1984 Supercritical water destruction of aqueous wastes. *Hazardous Waste* **1** (4), 453–467.

Whiting, P. 1996 Reversible flow supercritical reactor and method for operating same, U.S. Patent #5560823.

Whiting, P. 1997 Reversible flow supercritical reactor and method for operating same, U.S. Patent #5667698.