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SEPARATION OF BORIC ACID FROM PWR WASTE BY VOLATILIZATION DURING EVAPORATION

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ABSTRACT

SCK•CEN has developed a process to separate boric acid during and/or after evaporation of the liquid waste from pressurized light-water reactors. The key goal is to achieve higher waste volume reduction factors, while maintaining low activity discharge limits. An additional goal is to obtain purified boric acid for recycling. The process is based on the volatility of boric acid in steam. The liquid waste is treated in a semicontinuous evaporator, which operates preferentially at a higher temperature than the present evaporators. The stream loaded with boric acid is fed to a column for fractional condensation with partial reflux. In this way, one obtains a highly concentrated waste that contains all the radioactive and chemical impurities and little boron, a concentrated boric acid solution which can be reused, as well as a highly decontaminated effluent without boron. In case replacement or adaptation of existing evaporators is less practical, one can adapt the process for the treatment of evaporator concentrates. After having been intensively tested at SCK•CEN, the process has recently been demonstrated in a small pilot installation and with realistic liquid waste, at the nuclear power station in Doel, Belgium. The results corresponded to the theoretical predictions. After a transitional period, the boron concentration in the evaporator no longer increased and consequently did not limit the achievable waste volume reduction factor. The boric acid was recovered from the steam and during a supplementary treatment we recovered additional boric acid from the waste concentrate.

INTRODUCTION

The liquid waste of pressurized light-water reactor (PWR) plants contains substantial amounts of boric acid. In PWRs, boric acid is used as a soluble neutron poison to suppress and control the nuclear fission [1,2]. Dissolved boric acid is useful in case of a loss-of-coolant accident. Routinely it ensures subcritical conditions in the spent fuel pool and during refuelling. During reactor operation its concentration in the primary coolant is gradually decreased, mostly by dilution and withdrawal of the coolant, in order to compensate for the inherent long-term reactivity decrease. Because the thermal neutron induced reaction ^{10}B (n,α) ^{7}Li has a very high cross section, it captures the neutrons that would otherwise contribute to the nuclear fission reaction. Nevertheless, only a small fraction of the boron is effectively transformed into lithium. Usually, a large fraction is recovered from the reactor letdown stream and from other clean primary system wastes, and is then recycled. But much boric acid still ends up in the normally nonrecyclable low-level liquid waste (LLLW), in which it represents the largest constituent.

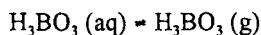
At many nuclear power plants, the evaporation of the LLLW guarantees high decontamination factors for the condensed vapour, which is essentially pure water [3]. Evaporation thus guarantees low releases of radioactivity, except for tritium. The relatively high boron concentration of the waste nevertheless limits the volume reduction factor for the evaporator residues. Furthermore, the presence of boric acid disturbs the conditioning process [4,5]. Conditioned and nonconditioned boron-containing evaporator concentrates represent an important fraction of the volume of low level nuclear waste. The escalating costs and provisions for the treatment, storage and disposal of this waste are proportional to its volume. A high volume reduction factor is thus highly desirable. After the international banning of sea dumping, shallow land disposal of nuclear waste is also being contested and limited. Nuclear power plant managers have introduced strict measures to limit the production of waste. A further volume reduction of the radioactive waste requires

the separation of boric acid from the radioactivity before, during or after the LLLW evaporation, as well as boron recycling, if possible. Separation of boric acid will also result in a waste that is less difficult to process and has a better long term stability [4,5].

Since 1992, SCK•CEN has been developing an original process for the separation of boric acid by volatilization during the evaporation of PWR LLLW [6]. The key goal is to achieve higher waste volume reduction factors in a cost-effective way, while maintaining low activity discharge limits. An additional goal is to obtain purified boric acid for recycling.

VOLATILIZATION OF BORIC ACID

Boric acid volatilizes in steam. A significant amount of boric acid can be found in natural steam vents in Tuscany, Italy [7]. The volatility is practically completely due to the undissociated acid [8]:



The experimental distribution coefficient D is defined as follows:

$$D = \frac{\text{mole fraction of boric acid in the vapour}}{\text{mole fraction of boric acid in the liquid}}$$

For practical reasons we have used the following approximation:

$$D = \frac{\text{weight fraction of boric acid in the vapour}}{\text{weight fraction of boric acid in the liquid}}$$

D is smaller than one. Its value depends mainly on the temperature. The pH affects the boric acid dissociation and thus the apparent D.

Boron volatilizes under the form of the undissociated acid H_3BO_3 and not significantly in the form of borate or polyborate. Dissociation can be taken into account defining a fraction α as:

$$\alpha = \frac{[H_3BO_3]}{[B]_{tot}}$$

The dissociation equilibria of boric acid are rather well known [10]. Our preliminary experiments confirmed the calculations in the literature [11], which show that, up to pH(25°C) 8, the apparent D is nearly independent of pH. Alkalization of the LLLW has thus to be avoided for the separation of boric acid by volatilization during evaporation.

The distribution coefficient is higher at higher temperature. The solubility of boric acid in water also increases strongly with increasing temperature. In most nuclear power plants, hot steam, up to a pressure of, e.g., 1 MPa (10 bar), is available as a very cheap heating medium. For our experiments we have therefore chosen an operating pressure of maximum 1 MPa. At the corresponding temperature, the volatility of the possible interfering impurity SiO_2 is still negligibly low [11].

D. G. Tskhvishvili and V. V. Galustashvili have investigated the volatilization of boric acid from its boiling solution in the pressure range of 0.2 to 20 MPa [12]. The presence of $NaCl$, Na_2SO_4 and iron oxides did not affect the value of the distribution coefficient. According to their results, the distribution coefficient for boric acid can be calculated with the following formula:

$$D = \frac{C_s}{C_w} \cdot \left(\frac{\rho_s}{\rho_w} \right)^{0.9},$$

where C stands for the boric acid concentration, ρ for the density and the subscripts s and w for steam and water, respectively. According to this formula, the distribution coefficient for boric acid at 175°C is 0.009. Interpolation of other experimental D values collected by P. Cohen yields slightly higher distribution coefficients ranging from 0.01 to 0.035 at 175°C [1].

It is also possible to estimate the value of the distribution coefficient at a certain temperature from the known solubility of H_3BO_3 [1] as well as the equilibrium vapour pressures of H_3BO_3 [13,14] and H_2O [11] at that same temperature. According to Raoult's law, we therefore assume, proportionality between the partial pressure of H_3BO_3 above a solution and the H_3BO_3 concentration in that solution. This corresponds to a constant distribution coefficient at constant temperature. Furthermore, we take into account the fact that the H_3BO_3 vapour pressure above a saturated H_3BO_3 solution equals the H_3BO_3 vapour pressure above solid H_3BO_3 at the same temperature (and dewpoint). According to this method, the higher defined distribution coefficient is about 0.008 at 175°C.

Finally, the distribution coefficient can be calculated from tabulated thermochemical data. According to J.W. Cobble and S.W. Lin, this leads to a value of about 0.015 at 175°C [11]. An analogous calculation with the HSC programme yields a distribution coefficient of 0.04 at the same temperature [14]. The calculations made no allowance for activity coefficients, which can lead to errors if strong electrolytes are involved [15].

SEPARATION OF BORIC ACID BY VOLATILIZATION DURING EVAPORATION

Because of its volatility, boric acid, together with the water, can be separated from nonvolatile radiochemical impurities during the evaporation. The process can be easily explained with the help of Figure 1.

The heart of the process is an evaporator which operates semicontinuously, i.e., with no removal of concentrated waste until the end of the considered time period. For modelling, the evaporator is supposed to have a constant liquid inventory, and the feed is supposed to have a constant flow rate and a constant composition. During operation, and as long as no concentrated waste is removed, the concentration of the nonvolatile impurities in the liquid in the evaporator increases linearly with the

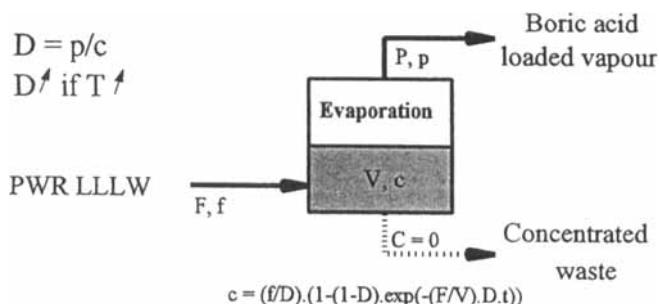


FIGURE 1. Separation of boric acid during volume reduction of PWR LLLW.

operating time. Within the evaporator, boric acid is distributed between the vapour phase and the liquid phase, as determined by the distribution coefficient D. Because the mole fraction of boric acid in the vapour phase is smaller than the mole fraction in the liquid phase, the liquid in the evaporator will also enrich in boric acid, but not linearly with time. There will be an asymptotic approach to the situation in which the boric acid concentration in the vapour that leaves the installation, equals the boric acid concentration in the feed, and in which the output of pure boric acid with the condensed vapour equals the input of contaminated boric acid with the PWR LLLW feed. A more quantitative treatment is given below.

Although not included in the following theoretical model, the vapour phase can be fed to a fractionating column. This allows to obtain a concentrated solution of pure boric acid for recycling and pure water for discharge.

The following symbols are used to explain the process:

F :	flow rate of the feed (PWR LLLW)	kg/h;
P :	flow rate of the condensed vapour (H_3BO_3 in water)	kg/h;
C :	flow rate of the concentrated waste	kg/h;
f :	boric acid concentration in the feed	ppm B;
p :	boric acid concentration in the vapour	ppm B;

c : boric acid concentration in the evaporator ppm B;
 V : liquid inventory of the evaporator kg;
 D : distribution coefficient of boron, definition : $D = \frac{P}{c}$ -;

F, P, C, f, V and D are constants.

For semicontinuous operation :

$$C = 0$$

$$\text{and } P = F$$

The boric acid balance over the evaporator can then be written as:

$$\frac{dc}{dt} = \frac{F}{V} \cdot (f - D \cdot c)$$

Integrating, and taking into account that $c = f$ at $t = 0$, gives the evolution of c (and p) as a function of time:

$$c = \frac{f}{D} \cdot [1 - (1-D) \cdot e^{-\frac{F \cdot D \cdot t}{V}}] \quad (1)$$

For the asymptotic situation, when $t = \infty$, this results in:

$$\begin{aligned} \lim_{t \rightarrow \infty} c &= \frac{f}{D} \\ \lim_{t \rightarrow \infty} p &= D \cdot c(t \rightarrow \infty) = f \\ \lim_{t \rightarrow \infty} (p \cdot P) &= f \cdot F \end{aligned}$$

A, the fractional approach to this asymptotic situation, is given by:

$$A = \frac{p}{f} = \frac{D \cdot c}{f} \quad (2)$$

On the basis of equation (1), the time to reach a given fractional approach to the asymptotic situation is given by:

$$t = \frac{V}{F \cdot D} \cdot \ln \frac{1-D}{1-A} \quad (3)$$

R, the volume reduction factor at time t, is given by:

$$R = \frac{F \cdot t}{V}$$

B, the overall fractional boron recovery in the condensed steam, is given by:

$$B = 1 - \frac{e \cdot V}{f \cdot F \cdot t + f \cdot V} \approx B = 1 - \frac{A}{D \cdot (R + 1)} \quad (4)$$

From the foregoing, one can deduce that the larger the experimental distribution coefficient, the better the results. The concentration of boron that remains in the inventory is smaller, as well as the time needed to reach the asymptotic situation.

A graphic representation of a case taken as example is shown in Figure 2. If $V = 0.5 \text{ m}^3$, $F = 1 \text{ m}^3/\text{h}$, $f = 100 \text{ ppm B}$ and $D = 0.007$ at 175°C , then the time to reach 95% of the asymptotic value, as given by the formula (3), equals 213.5 hours. At that time the volume reduction factor is 427 and practically all the boron that comes in leaves with the product P ($p = f$). The boron concentration in the evaporator, which remains constant after this point, equals 14286 ppm B in this example. The boron concentration in the evaporator remains high in comparison with the boron concentration of the steam leaving the evaporator, yet the total amount of boron that is removed from the concentrate soon exceeds that which remains in the concentrate. This is represented in Figure 3.

BENCH-SCALE TESTS

The main purpose of our bench-scale experiments was to test the feasibility of the new process on simulated and real LLLW in a small but integrated installation. At the same time the experiments should provide practical values for the distribution of boric acid and major impurities. The bench-scale installation had a maximum throughput of 0.5 kg/h. Its main component was a semicontinuous evaporator, operating at a constant temperature of about 175°C and with a constant liquid inventory of about 0.375 kg. A metering pump transferred the feed into the evaporator. The vapour phase left the evaporator through a demister and via a control valve. These latter parts were also heated at 175°C to avoid premature condensation and reflux.

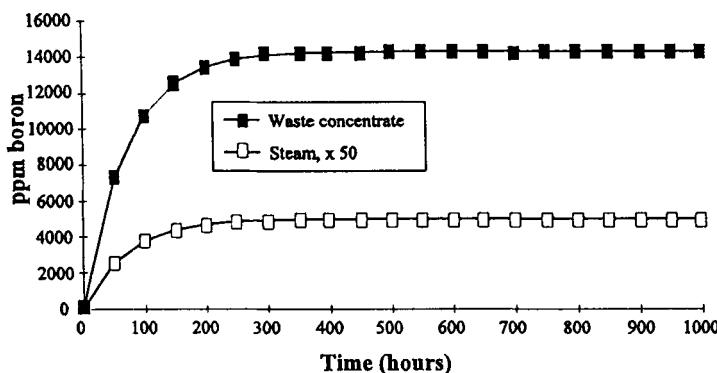


FIGURE 2. After an initial period, all the boron that comes in leaves with the steam.

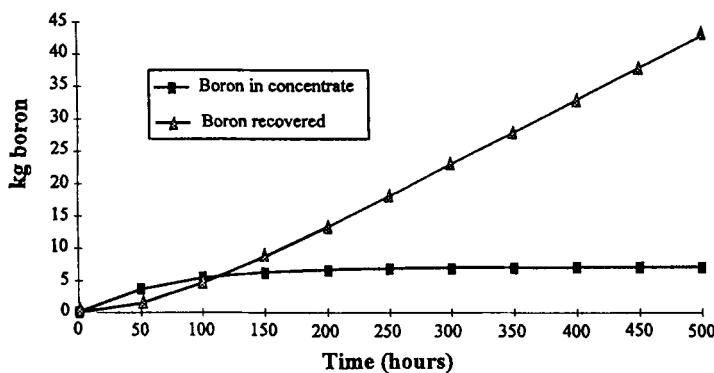


FIGURE 3. The total amount of recovered boric acid increases with time.

The distribution coefficients were checked during preliminary short tests. The evaporator was filled with boric acid solutions of different concentrations (500 to 10000 ppm B) and different pH (4 to 9), and water was used as the feed. In fact, we used real PWR LLLW to which we added extra boric acid and H_2SO_4 or NaOH . The vapour was simply condensed and its boron content was compared with the boron content of the solution in the evaporator. After complexation with glycerol,

we analysed boric acid by titration with NaOH [16,17]. Except for the test at pH = 9, all the distribution coefficients are between 0.005 and 0.008.

For the integrated long duration tests, the feed was simulated LLLW or real LLLW. In this case we recovered the separated boric acid. The produced vapour was passed through a heated bubbler with a constant liquid inventory of about 0.25 kg, and through a reflux column on top of the bubbler. Afterwards it was condensed. The feed, the evaporator concentrate, and several samples from the concentrated boric acid in the bubbler and from the distillate were analysed for boric acid, impurities, and radioactivity. We monitored the water and boron balances by weighing and titrating. The radiochemical and chemical impurities were measured by γ -ray spectrometry and by inductively coupled plasma atomic emission spectroscopy (ICP AES), and ion-exchange chromatography (IC), respectively. Some results of an experiment on about 160 kg genuine PWR LLLW are given in Table 1. More details and results of other experiments are available in a report [18]. This LLLW contained 181 ppm boron as boric acid. The pH was 6.8 at 25°C. The total activity of the γ -ray emitting radionuclides, mainly ^{60}Co , ^{58}Co , ^{137}Cs and ^{54}Mn , was 11 Bq/g. The water was grey-black because of the presence of suspended solid material, and it smelled unpleasantly. The most important ions were Na^+ (62 ppm), $\text{H}_x\text{PO}_4^{(3-x)}$ (54 ppm), Cl^- (24 ppm) and SO_4^{2-} (16 ppm).

In general, these experiments lead to the following conclusions:

- The water, boron and most other balances were in equilibrium, but some radionuclides stuck to the wall of the evaporator.
- The activity of the discharged distillate was always below the detection limit of 0.01 MBq/m³ (SCK•CEN), which corresponded to a minimum decontamination factor of up to 1000.
- After a certain time, there was nearly no further accumulation of boron in the evaporator concentrate.
- The volume reduction factor for the radioactive evaporator concentrate did not

TABLE I. SUMMARIZED RESULTS OF A BENCH SCALE EXPERIMENT.

Operating Time (hours)	Volume Reduction Factor	Boric Acid Recovery	Boric Acid Removal	D(H_3BO_3) (Integral)
44.0	82	17.0%	22.2%	0.0066
68.0	125	21.7%	27.1%	0.0055
140.0	242	32.2%	37.7%	0.0043
188.5	319	41.1%	47.5%	0.0047
235.5	392	47.2%	54.4%	0.0048
309.0	500	49.3%	57.5%	0.0042
355.5	568	46.5%	55.5%	0.0035
404.0	633	54.3%	63.7%	0.0041

depend on the boric acid content of the feed. In fact, it was limited by the available amount of LLLW.

Although nearly all chemical and radiochemical impurities remained in the evaporator concentrate, the purity of the recovered concentrated boric acid solutions was insufficient for direct recycling.

PILOT-SCALE TESTS

After the promising bench-scale experiments, we constructed a small pilot installation for a further volume reduction of PWR LLLW by volatilization of boric acid during evaporation at elevated temperature and pressure. The pilot installation had the same components as the bench-scale installation, but it was capable of processing up to 10 kg/h. After cold testing at SCK•CEN, it was installed at the nuclear power plant in Doel, Belgium. The evaporator was an adapted, stainless steel steam generator, which could operate at a pressure of up to 1.1 MPa. It was provided

with a sampling system and with the necessary shielding. In a glass atmospherical distillation unit, the boric acid was concentrated with a view to possible recycling.

A scheme of the installation is shown in Figure 4. After automatic adaptation of the pH to a value of 6.5, the LLLW is fed into the evaporator (EVAP). The metering pump for the feed is regulated to maintain a constant level in the evaporator, whereas the electric heating of the evaporator is regulated to obtain and to maintain the desired pressure of 0.9 MPa as well as the corresponding temperature of nearly 180°C. The steam produced in the evaporator contains boric acid but is free from radiochemical and chemical impurities. After expansion, the steam is fed into an atmospherical distillation unit (DIST), where the boric acid gets concentrated in the reboiler and the effluent gets condensed. Because of the low volatility of boric acid at the atmospherical boiling point of the solution, a low reflux ratio in the atmospherical distillation column suffices to guarantee a very low boron concentration in the distillate. In this way, the incoming waste stream is split into three streams:

- a radioactive waste concentrate containing almost all the radiochemical and chemical impurities together with some boron;
- a concentrated boric acid solution that can be reused if it is sufficiently pure;
- an effluent with a very low boron content and which is highly decontaminated.

The commissioning of the pilot installation and preliminary testing posed no particular problems. Also the demonstration experiment itself went fluently, apart from a few automatic shutdowns, due to foaming in the atmospherical distillation unit. This forced us to operate the installation at a limited throughput of only 6 kg/h instead of 10 kg/h. On the other hand, we could not decrease the operational liquid inventory of the evaporator containing 21 litres.

The demonstration experiment was split into two phases. During a first phase, approximately 11000 kg LLLW were treated as described before. Because of the

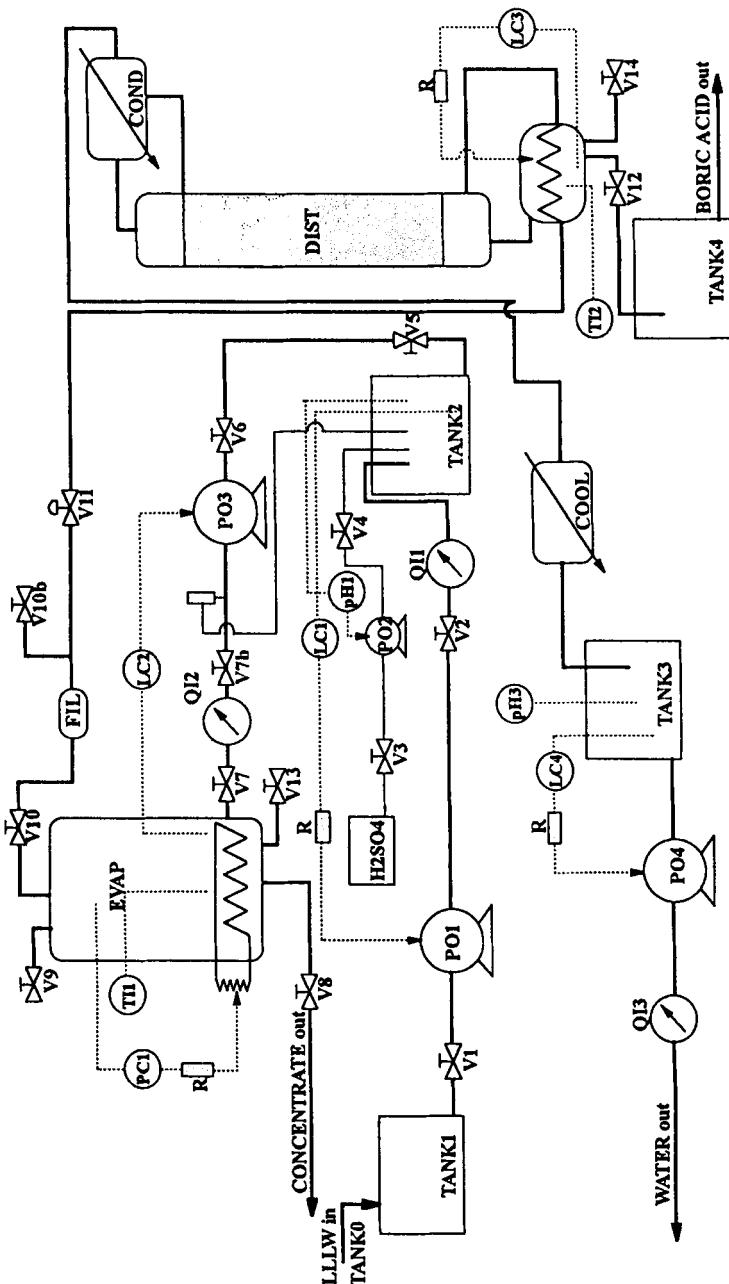


FIGURE 4. In the pilot installation, boric acid is volatilized during the evaporation (EVAP) of the low-level liquid waste, and it is recovered at the bottom of an added distillation column (DIST).

small throughput-to-inventory ratio, it took a long time to achieve the target waste volume reduction factor of 500. Each time the boric acid concentration in the reboiler had reached a concentration above 6000 ppm boron, it was replaced by demineralized water. The LLLW feed, as well as samples regularly taken from the waste concentrate in the evaporator, from the boric acid solution in the reboiler and finally from the effluent distillate, were analysed in the same way as for the bench-scale tests. The chemical and radiochemical composition of the LLLW are given in Table 2 and Table 3, respectively.

During a shorter second phase, the boron was further removed from the radioactive concentrate without adding additional LLLW. During that second phase the decontaminated, purified and boron-free distillate from the atmospherical unit was recycled and used as feed for the evaporator, instead of LLLW. This allowed us to achieve a boron removal of more than 80%, however, without further increase of the volume reduction factor. Furthermore, by this means we were able to demonstrate the feasibility of treating evaporator concentrates.

At the end of the first phase of the demonstration experiment, the waste volume reduction factor was about 549. We then passed on to the second phase, mainly because we had used up our 11000 kg LLLW stock and because no more LLLW with the same composition was available. Figure 5 shows the amount of boron in each stream during the first and second phase. Within a 5% error range, the boron balance was always in equilibrium. About 71% of the 600 g boron which entered the pilot installation was removed from the waste concentrate at the end of the first phase, and 96% of this removed boron was recovered as a concentrated boric acid solution.

The process behaved as expected theoretically. For each sample taken from the evaporator, equation (1) allowed one to calculate the H_3BO_3 distribution coefficient the measured concentration of boron in that particular sample. Throughout the

TABLE 2. CHEMICAL COMPOSITION OF THE LLLW USED FOR THE PILOT-SCALE EXPERIMENT.

Element	ppm	Element	ppm	Element	ppm	Element	ppm
B	54.5	Ni	0.047	Rb	n.d.	Cl ⁻	19.2
Na	37	Ba	n.d.	Zn	0.02-0.05	PO ₄ ³⁻	106
K	8.6	W	0.01-0.02	Sc	n.d.	F ⁻	0.31
Si	1.76	Mo	0.066	Cr	0.01-0.02	HCOO ⁻	n.d.
Ca	7.6	Li	0.02-0.05	Sb	n.d.	NO ₂ ⁻	n.d.
Mg	2.14	Mn	1	Ti	0.02-0.05	SO ₄ ²⁻	23.2
Al	0.043	Fe	n.d.	Cu	0.01-0.02	NO ₃ ⁻	n.d.

TABLE 3. RADIOCHEMICAL COMPOSITION OF THE LLLW USED FOR THE PILOT-SCALE EXPERIMENT.

Isotope	MBq/m ³	Isotope	MBq/m ³
⁵⁴ Mn	0.054	¹²² Sb	0.051
⁵⁸ Co	0.198	¹³⁴ Cs	0.083
⁶⁰ Co	0.565	¹³⁷ Cs	0.085

experiment, the distribution coefficient was reasonably constant. The average value of D at the operating temperature of nearly 180°C was 0.0072, with a standard deviation of 0.0008. Combination of equations (4) and (1) yields a theoretical expression for the evolution of the fraction of boron removed:

$$B = 1 - \frac{V}{D.(F.t + V)} \cdot (1 - (1 - D) \cdot e^{-\frac{D.F.t}{V}}) \quad (5)$$

At each sampling, this fraction was determined from the measured boron concentrations in the reboiler and in the distillate. The experimental data are shown

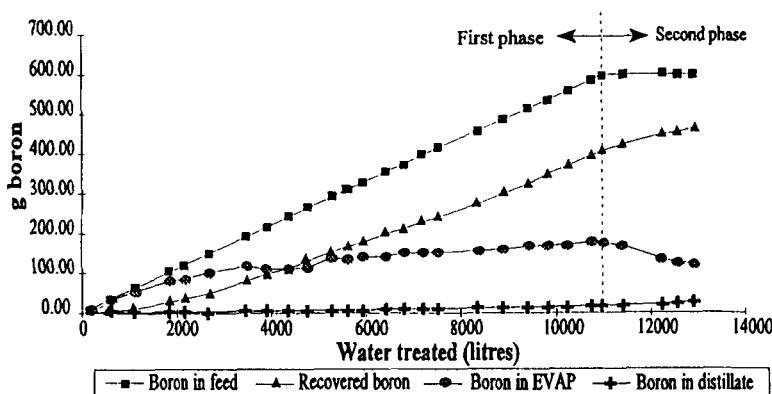


FIGURE 5. The pilot scale experiment demonstrated the separation and recovery of H_3BO_3 during the evaporation of LLLW (first phase) and the further recovery of H_3BO_3 from the evaporator concentrate (second phase).

in Figure 6. Fitting these data with equation (5) yielded a distribution coefficient of 0.0070, which compared well with the independently calculated value of 0.0072.

During the second phase, no more LLLW was added, but boric acid was further transferred from the evaporator into the reboiler of the atmospherical distillation unit, as shown in Figure 5. As expected, the efficiency of this process decreased with the decrease of the boron concentration in the evaporator. At the end of this phase, 82% of the original boron content had been removed from the evaporator concentrate, and 95% of the removed boron, i.e., 78% of the total amount of boron, had been recovered.

The radiochemical and chemical impurities accumulated in the waste concentrate in the evaporator. The specific activity of the distillate was always below the detection limit of 0.03 MBq/m³ (NPP Doel). The total activity of the recovered boric acid was 0.13 MBq. Nearly 99% of the original activity remained in the evaporator.

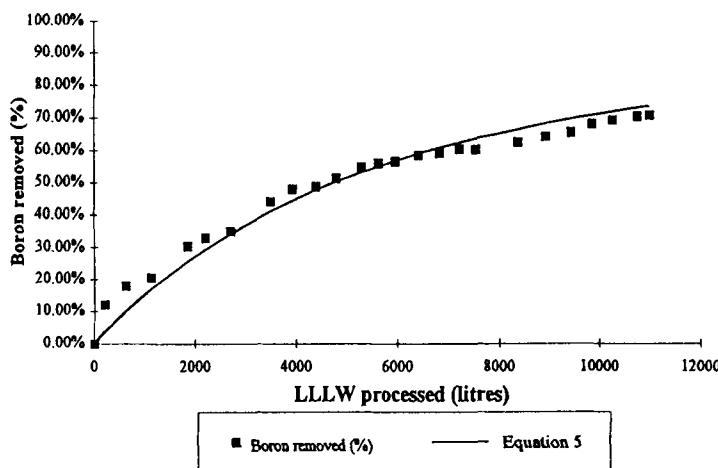


FIGURE 6. The results of the pilot-scale test corresponded to the theoretical predictions. At the end of the first phase, about 70% of the H_3BO_3 had been separated and recovered.

Except for silica, the concentration of all chemical impurities in the distillate was below 1 ppm. The main impurities in the recovered boric acid were Na, K, Si, Cl^- , $\text{H}_x\text{PO}_4^{(3-x)}$ and SO_4^{2-} . In general, the recovered boric acid contained 2 to 3% of the original amount of these impurities in the feed LLLW. This rather high values are probably due to entrainment. For radionuclides such as the Co isotopes, which tend to associate with solid particles or vessel walls, entrainment was lower. The total amount of Si in the recovered boric acid and in the distillate was much higher than the original amount in the LLLW feed. This is probably due to contamination from the quartz heating elements in the atmospherical distillation unit and from the glass distillation unit itself.

Summarizing, the pilot tests at the Doel nuclear power station allowed us to demonstrate the new process with realistic LLLW. From a technical point of view, the installation performed rather well, although some ameliorations still need to be

done. In comparison with our pilot installation, an industrial installation should be optimised to avoid foam formation in the distillation unit and to avoid entrainment in the evaporator. Construction materials should be chosen to avoid the silica contamination of the recovered boric acid. The throughput-to-inventory ratio should be much higher in order to shorten the length of a campaign. Furthermore, a lower liquid inventory will limit the total amount of radioactivity in the evaporator. Finally, the treatment of evaporator concentrates will consume less energy if the distillation column also operates at elevated pressure, and if the boron-free steam is recycled into the evaporator-contactor without condensation.

From the process point of view, the installation performed as one theoretically had expected for a boric acid distribution coefficient of about 0.007. The waste volume reduction factor was no longer limited by the boron concentration in the evaporator, which stabilized around 8000 ppm. We stopped the experiment with an impressive volume reduction factor of 550, yet below the maximum achievable value, which is determined by other components or possibly by the maximum allowable specific activity of the residue. Except for tritium and a silica contamination, the effluent was radiochemically and chemically pure water. 78% of the boric acid was recovered in the form of a 7000 ppm boron solution, which could be further purified for recycling.

CONCLUSIONS

The evaporation of an acid to neutral boric acid solution produces vapour with a boron content determined by the boric acid content of the solution and by the boric acid distribution coefficient. This coefficient increases with increasing temperature and is about 0.007 at 175°C. On the basis of these observations, SCK•CEN designed and tested a new process for the separation of boric acid during evaporation.

In comparison with the present evaporation practice for boron containing low-level liquid waste at pressurized light-water reactor plants, this process allows to

achieve higher waste volume reduction factors while maintaining low activity discharge limits. At the same time, it produces a concentrated boric acid solution for recycling into the plant. The main components of the installation are an evaporator, operating at e. g. 175°C, and a fractional condensation column. No chemicals have to be added, and even the current addition of alkali should be omitted. There is also no production of any secondary waste. In some nuclear power plants one could consider an adaptation or replacement of the existing evaporators. In other cases, one could apply an adapted version of the process for the treatment of evaporator concentrates.

During bench-scale experiments, and especially during the pilot scale demonstration at the Doel nuclear power plant, the process was successfully tested with normally nonrecyclable liquid radioactive waste. The results corresponded to the theoretical predictions. After a transitional period, the boron concentration in the evaporator no longer increased and consequently did not limit the achievable waste volume reduction. Fractional condensation of the steam allowed us to recover the boric acid that did no longer accumulate in the evaporator. With a supplementary treatment, we also recovered boric acid from the evaporator concentrate. In order to be recycled into the primary coolant, the recovered boric acid will probably need further purification, as was the case in our tests. On the other hand, if only a further waste volume reduction is required, one could omit the last step of the process and discharge the decontaminated diluted boric acid.

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REFERENCES

1. P. Cohen, Water Coolant Technology of Power Reactors, 2nd printing, American Nuclear Society (1980).
2. S. Glasstone and A. Sesonske, Nuclear Reactor Engineering, 3rd edition, Van Nostrand Reinhold, New York (1981).
3. S. Santraille et al., in Radioactive Waste Management and Disposal, L. Cecille Ed., Elsevier Applied Science, London and New York, 1991, p.25.
4. H. Matsuzuru and N. Moriyama, Nuclear Science and Engineering 80, 14 (1982).
5. J. Jeffrey, L. Garner and W. House in Waste Management '91, Vol. 1, R.G. Post Ed., American Nuclear Society, USA, 1991, p.359.
6. A. Bruggeman and J. Braet, Method for Separating Boric Acid, Belgian Patent 9300608 (1993), International Patents Applied for.
7. W. A. Gale, in Boron, Metallo-Boron Compounds and Boranes, R. M. Adams Ed., Wiley Interscience, New York, 1964, p.1.
8. D. E. Byrnes, Some physicochemical Studies of Boric Acid Solutions at High Temperatures, Report WCAP-3713, Westinghouse Electric Corporation, Atomic Power Division, Pittsburgh, Pennsylvania, USA, 1962.
9. J. Bosholm, VGB Kraftwerkstechnik 74, 5, p. 396 (1994).
10. R. E. Mesmer, C. F. Baes, Jr, and F. H. Sweeton, Inorganic Chemistry, 11, 537 (1972).
11. J. W. Cobble and S.W. Lin in ASME Handbook on Water Technology for Thermal Power Systems, P. Cohen Ed., ASME, USA, 1989, p. 551 (chapter 8).
12. D. G. Tskhvishvili and V. V. Galustashvili, Soviet. At. Energy, 16, 1, p. 70 (1964).
13. M.v. Stackelberg, F. Quatram and J. Dressel, Ztschr. Elektrochem., 43, 1, p. 14 (1937).
14. A. Roine, HSC Chemistry for Windows ver. 2.03, Outokumpu Research Oy, Finland (1994).

15. J. W. Cobble, San Diego State University, San Diego, California, USA, personal communication, 1995.
16. A. I. Vogel, A Text-book of Quantitative Inorganic Analysis, 3rd Edition, Longman, London (1961).
17. A. A. Nemodruk and Z. K. Karalova, Analytical Chemistry of Boron, Academy of Sciences of the USSR (1964), Israel Program for Scientific Translations, Jerusalem (1965).
18. J. Braet, A. Bruggeman and F. Smaers, Advanced Processes for the Treatment of Low Level Liquid Wastes at a Pilot Plant Scale.
Boron Separation from LLLW: Volatilization at Elevated Temperature and Pressure, Report R-3048, SCK•CEN, Mol, Belgium (1995).