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BORATE COMPOUND CONTENT REDUCTION IN LIQUID RADIOACTIVE WASTE FROM NUCLEAR POWER PLANTS WITH VVER REACTOR

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ABSTRACT

This paper describes the current status of liquid waste (evaporator concentrates) inventory at V-1 and V-2 NPPs in Jaslovske Bohunice and the intention to separate boron from them with respect to waste minimisation and improvement of physical and chemical properties for further waste treatment and conditioning. Preliminary results of laboratory experiments concerned to borate crystallisation after pH adjustment with nitric or formic acid performed in the 1998 are given. At the present time laboratory experiments continuing - next acids, coagulation with carbon oxide, electrolytic process, ion exchange resin, study of decontamination factors, immobilization of boric acid, decrease radioactivity, purification of boron-contained compounds. Slovenske Elektrarne have accumulated 7,000 m^3 of evaporator concentrates containing 100-180 g/l borate. In order to make more storage space available, it is proposed to remove some of the borate in the liquor by precipitation as sodium tetraborate and immobilise in either cement of bitumen. The supernate can be further volume reduced by evaporation and returned to the tanks. Slovenske Elektrarne are currently evaluating acid addition to the pH 12-13 concentrate to reduce the borate solubility. However, this adds to the salt burden of the waste through this chemical addition -thus creating future increases in conditioning and disposal costs. Boric acid is used in pressurized water as a soluble neutron poison to control reactivity and also to assure a safety margin in the spent fuel pool and during refuelling operations. Boric acid is also present in the water reserved for injection into the reactor in the event of postulated accidents.

1 INTRODUCTION

During operation of V-1 and V-2 NPPs in Jaslovske Bohunice arises liquid radioactive waste, currently stored as concentrate in storage tanks after evaporation. Minimisation of waste production by the means of separation of boron-contained compounds is one of the possible ways to improve effectiveness of NPPs operation. Boric acid and boron-contained compounds are main part of some liquid waste streams arising in PWR NPPs and significantly influence chemical properties of waste streams and subsequent possibilities of radioactive waste treatment. Evaporator concentrates contain of 150 - 400 $kg.m^{-3}$ dissolved salts, in which boron is presented in the form of various anionic species in the total amount of 60 - 160 kg.m^{-3}. Boron-containing anionic species negative affect a process of waste solidification and deteriorate properties of final waste products. Inhibiting effect of boron species on cementation is so significant, that the concentration slightly higher than in concentrates may stop the process of stiffening and hardening of cementitious rock. During bituminization, generally performed at the temperature of approximately 180°C, boron anionic species may form high viscous and abrasive polymer substances. Their adhesion to metallic surface is so high, that they are formed also in rotary film evaporator, where bituminization process run in very thin layer. One of the ways to avoid mentioned problems is decreasing of boron content in waste to be solidified.

When boric acid should not be separated before waste concentrating and / or treatment for final disposal, final volume of packed waste should be substantially higher. Removing of boric acid from liquid radioactive waste streams may decrease final waste volume in magnitude of one order and significantly reduce the cost of the waste disposal. Boric acid separation technology for the liquid waste streams must by considered carefully as it means additional investment, equipment and corresponding operational demands. But significance of boric acid separation both for recycling (or reuse) or improvement of waste treatment for disposal from the point of view financial, technical and environmental impacts is evident [1].

The decision to deal with separation of boric acid from evaporator concentrates results from the fact that there are 3344 m^3 (V-1 NPP) and 2476 m^3 (V-2 NPP) of evaporator concentrates (referred to 120 kg.m^3 boric acid level) in storage tanks at present and growing cost of waste treatment, storage and disposal (chemical composition of stored radioactive concentrates is given in Table I). Both NPPs are already in operation for a long time and changes in technology leading to significant reduction of boric acid in radioactive wastewater should be very difficult to realise. Administrative actions are main control tools at present. This means, no ad-lib separation method should be implemented in NPPs Jaslovske Bohunice. Selection of separation technology should reflect both specific features of current technology and accumulated volume of liquid radioactive concentrates.

Subtask Separation and Recyclation of Boric Acid from Waste Streams is running under task Evaluation and Optimisation of water chemistry of NPPs with primary objectives as follows:

Review of current world trends in separation, recyclation, or treatment of boric acid containing liquid waste streams from NPPs
Evaluation and optimisation of laboratory procedures for non active model NPP concentrates
Extension of laboratory experiments to real active concentrates

Proposal of suitable technology applicable for NPPs Jaslovske Bohunice concentrates.In the first stage of subtask the literature survey and experimental works were focused on the following topics:

Review of boric acid separation technologies world wide used and choice of potentially available technology for application in NPPs Jaslovske Bohunice
Inventory and characterisation of liquid wastes in NPPs Jaslovske Bohunice
Laboratory experiments concerned to pH treatment with various acids (nitrous and formic acids), crystallisation of borates and evaluation of separation efficiency of borate removal from model NPP concentrates.

This paper presents preliminary results of laboratory experiments carried out in the 1998.

Table 1 Chemical composition of evaporator concentrates in storage tanks at NPPs Jaslovske Bohunice

Parameter	V-1 NPP	V-2 NPP
pH	11,3 – 13,3	11,2 – 13,2
Conductivity [mS/cm]	76,5 – 105,2	63,6 – 126,6
Boric Acid [kg .m^{-3}]	73 – 160	64,0 – 117,0
Salt content [g/l]	150 – 397	150 – 321
Na^+ [g/l]	42 – 100	25,3 – 75
K^+ [g/l]	9,4 – 21,5	9,1 – 2,6
Cl^- [g/l]	0,9 – 1,8	1,1 – 1,8
NO_3^- [g/l]	5,0 – 29,6	–
SO_4^{2-}[g/l]	1,9 – 3,4	–
Organic substances [g O_2/l]	14,5 – 34,8	0,6 – 5,6
^{110m}Ag [Bq/l]	1.10^4 – $3,1.10^5$	–
^{60}Co [Bq.l^{-1}]	$3,0.10^4$ – $1,1.10^6$	$4,7.10^2$ – $2,7.10^4$
^{134}Cs [Bq.l^{-1}]	$8,2.\ 10^4$ – $2,0.10^6$	$1,3.10^3$ – $1,9.\ 10^4$
^{137}Cs [Bq.l^{-1}]	$1,3.10^6$ – $8,4.10^6$	$3,6.10^4$ – $2,9.10^5$
^{54}Mn [Bq.l^{-1}]	$1,3.10^3$ – $5,0.10^5$	$4,1.10^2$ – $3,6.10^3$

2 EXPERIMENTAL

Preparation of model NPP V1 concentrates. Model solution of V1 concentrates was prepared by diluting of reagents according to Table 2 [2].

Table 2 Chemical composition and physico-chemical characteristics of model V-1 NPP concentrates

Reagent	Content
NaOH [g.l^{-1}]	72.9
KOH [g.l^{-1}]	14.9
H_3BO_3 [g.l^{-1}]	76.0
Na_2SO_4 [g.l^{-1}]	3.5
$NaNO_2$ [g.l^{-1}]	1.5
$NaNO_3$ [g.l^{-1}]	27.1
NaCl [g.l^{-1}]	2.0
$C_6H_8O_7$ [g.l^{-1}]	1.6
$C_2H_2O_4 .2H_2O$ [g.l^{-1}]	2.8

Physico-chemical characteristics	Value
pH	13.3
Specific mass [g.cm^{-3}]	1.414
Residue after 24 hour treatment at 105 - 110 °C [%]	15.3
Salt content [g.l^{-1}]	174.6

Temperature and pH measurement. Values of pH and temperatures were obtained by the reference pH-meter Methrom 713 (Methrom, Herisseau, Switzerland) equipped with combined electrode and thermo-couple.

Boric acid determination. Boric acid in samples of model concentrates was determined spectrophotome-trically with azomethine-H [3].

Statistical analysis. Obtained results were statistically analysed using Statgraphics Plus for Windows version 2.1 (Manugistics Inc., Rockville, USA).

Experiment I. To the 100 ml of concentrate model solution nitric or formic acid was added and after reaching equilibrium changes of pH and temperature were measured. Investigated pH range was of 6 to 12 pH units.

Experiment II. Similarly as in experiment I, but pH of solutions was adjusted with nitric acid to 8, 8.5 and 9 and with formic acid to 8.5 and 9. Arose crystals were after 96 hour settling separated by filtration and weighted after air drying. In obtained crystals were analysed for boron (as boric acid).

3 RESULTS AND DISCUSSION

Experiment I

Primary objective of this experiment was to find relationships between pH changes due to addition of nitric or formic acid (titration curves). Addition of acids to concentrate model solutions is exothermic reaction and therefore the thermal effects were also investigated. Obtained results indicated optimum conditions for rising of reproducible yields of precipitation in the range of 9 to 10 pH units (close to pK_a value of boric acid) and higher hydration heat in the case of nitric acid than formic acid. These facts lead to suggestion that reaching of equilibrium after adding of acid should be prolonged in the case of nitric acid compared to formic acid.

Experiment II

After evaluation of Experiment I results, this experimental part was focused on investigation of precipitation yield by the treatment with both tested acids in pH range of 8 to 9, study of precipitation yields as the function of time, and used pH-adjuster. Equivalence of precipitation evaluation by the means of gravimetry, content of boron and boric acid was investigated too.

Mean values of yields and H_3BO_3 contents obtained at various pH values by treatment with nitric or formic acid are given in Table 3 (experiments were performed in triplicate). Calculated results reflect random error propagation [4] and are corrected for volume changes due to acid addition. From the table it follows that for both acid highest yields were obtained at pH value 9 when were removed approximately 72 % of boric content of concentrate model solution and yields were independent of acid used for pH adjustment. Mass balance revealed that 3 up to 10 % of total content of boric acid to be loosing during separation process and / or due to systematic error of used analytical methods.

In addition, the relation between yield of crystals and determined amount of boric acid in yield was investigated. Primary objective was to clarify equivalency of separation process evaluation according to both parameters. Statistical analysis by the means of linear regression has show close correlation between investigated parameters and resulting equivalence of separation process efficiency evaluation on the basis of gravimetric and /or boric acid content in yield. Correlation coefficients were higher than 0.99 and slopes of regression lines were in the range of 0.48 – 0.53 for both acids and pooled data).

Table 3 Yield of crystals, H_3BO_3-content in yield and filtrate, separation efficiency for H_3BO_3 and mass balance for H_3BO_3 after addition acids

Addition HNO_3			
	pH 8	pH 8.5	pH 9
Yield [g]	4,44 ± 0,25	8.70 ± 0,81	10,00 ± 0,37
H_3BO_3 content in yield [g]	2,33 ± 0,11	4,59 ± 0,38	5,31 ± 0,34
Separation efficiency [% H_3BO_3]	30,7	60,4	69,9
H_3BO_3 content in filtrate [$g.l^{-1}$]	42,33 ± 1,77	25,47 ± 0,58	14,23 ± 0,76
Sum of H_3BO_3 in yield and filtrate [g]	6,98 ± 0,22	7,38 ± 0,38	6,85 ± 0,35
Balance of H_3BO_3 [%]	91,9	97,1	90,2
pH after crystallisation	8,00 ± 0,61	8,17 ± 0,10	8,99 ± 0,06

Addition HCOOH			
	pH 8	pH 8.5	pH 9
Yield [g]		8,47 ± 0,18	10,77 ± 0,12
H_3BO_3 content in yield [g]	–	4,38 ± 0,07	5,49 ± 0,11
Separation efficiency[% H_3BO_3]	–	57,6	72,2
H_3BO_3 content in filtrate [$g.l^{-1}$]	–	27,97 ± 0,25	14,07 ± 0,42
Sum of H_3BO_3 in yield and filtrate [g]	–	7,36 ± 0,08	6,98 ± 0,11
Balance of H_3BO_3 [%]	–	96,8	91,8
pH after crystallisation	–	8,11 ± 0,09	8,77 ± 0,06

4 CONCLUSIONS

From the obtained results, following conclusions may be derived:

Optimum pH for boric acid separation from concentrate model solutions is form the region of 9 to 10.

Higher heat generation should be when nitric acid is used for pH adjustment. This may result in longer duration to reach equilibrium state. Longer duration should be expected also when pH adjustment of solution will be performed without stirring and slow diffusion processes take a place in solution.

Highest separation efficiency (approx. 72%) was observed at pH value of 9 and was independent of pH-adjuster used.

Mass balance revealed a loss of 3 up to 10 % of boric acid.

Evaluation of separation process on the basis of gravimetrically determined yield and content of boric acid in yield is equivalent.

Future laboratory experiments will be focused on optimisation of crystallisation process to obtain reproducible and maximal yields of borates, acceleration of steady state in solution, morphology of crystals and evaluation of qualitative characteristics of final products both with model and active concentrates. Later, experiments with real concentrates should be performed. Alternatively we suppose to carry out laboratory experiments concerned to electrochemical adjustment of pH by removing of sodium and potassium with subsequent crystallisation of borates. Ion exchange column for removing of ^{60}Co and ^{134,137}Cs should be added for experiment with active concentrates.

5 REFERENCES

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