

CONCENTRATION OF BORON IN LEACHATES AND INVESTIGATION ON THE TREATMENT METHOD

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SUMMARY:As part of the study, the Landfill Systems & Technologies Research Association of Japan, NPO, conducted research and investigations focusing on non-regulated substances in the leachates of landfill sites. Six substances, nitrate nitrogen, nitrite nitrogen, fluorine, boron, antimony, and selenium, were measured in leachates and treated sewage at twenty landfill sites in Japan. The measurement results indicated that the levels of the substances were low in leachates and treated sewage of most landfill site, but the levels of boron in leachates and treated sewage were somewhat high at some landfill sites. Therefore, a follow-up survey was conducted for boron. The results of comparison between leachates and treated sewage revealed that boron cannot be removed at existing wastewater treatment facilities. A test using chelate-adsorbed resin was conducted and good result were obtained. In addition, inclusion and elution tests for boron on disposed waste and topsoil were performed to trace the pathway of boron. The results indicated that boron in leachates is derived from landfill waste.

1. INTRODUCTION

Recently, environmental conservation has been discussed from a global viewpoint, with many international conferences being held. In Japan, more stringent environmental quality standards have been established for air, water, and soil. The general public has developed an interest in the environment and has raised concerns about the environmental impacts of unknown chemicals, while various organizations are providing information on dioxin, endocrine disrupting chemicals, and other pollutants.

Our group has focused investigations on the actual conditions of non-regulated substances in leachates at landfill sites. We studied 6 substances including non-regulated substances that will

be regulated in the near future and regulated substances that will be regulated more strictly. The substances are nitrate nitrogen, nitrite nitrogen, fluorine, boron, antimony, and selenium. Impressively, during our studies, effluent standards for 4 substances were established in July 2001, and only antimony remains unregulated. From these facts, we have come to believe that our studies are important.

2. THE CURRENT TREND OF REGULATIONS FOR 6 SUBSTANCES

2.1 Nitrate nitrogen and nitrite nitrogen

Sources of nitrate nitrogen and nitrite nitrogen in leachates are organic landfill materials such as sludge and waste. These are oxidized or reduced chemically/microbiologically in landfills, and generate ammonia nitrogen, nitrite nitrogen, and nitrate nitrogen.

In Japan, effluent standards for these designated hazardous substances were established in July 2001. The effluent standards define the maximum permissible limit as the sum of the amount of nitrite nitrogen, the amount of nitrate nitrogen, and the value calculated by multiplying the amount of ammonia nitrogen by 0.4; the limit is 100 mg/L.

2.2 Fluorine

Fluorine is used in the metal, semiconductor, and ceramic industries. With the exception of fluorine originating from nature, its source is considered to be sludge generated by liquid waste treatment processes for disposal by these industries.

Effluent standards for fluorine were also established in July 2001. The maximum permissible level is 15 mg/L in sea areas and 8 mg/L in other areas.

2.3 Boron

Boron is used in cosmetic items, soap, glass, and ceramics, as well as in medical fields. Boron in leachates originates from incineration ash, FRP products, glass, ceramics, etc. The elution mechanisms of boron are complex, and it has been reported that some forms of boron are difficult to elute.¹⁾

Effluent standards for boron were also established in July 2001. The maximum permissible level is 230 mg/L in sea areas and 10 mg/L in other areas. In addition, some local governments define local effluent standards more stringently than national standards; the limit is 2 mg/L or below.

2.4 Antimony

Antimony is commonly used as a flame retardant synergist, and is mixed in plastic, rubber, and fiber products. This suggests that antimony in leachates originates from landfill materials.

An effluent standard for antimony is not currently defined, but antimony is specified as a substance to be monitored.

2.5 Selenium

Selenium is used in electronic components, coloring agents for glass and ceramics, curing agents for rubber, insecticide, shampoo, etc. This suggests that selenium in leachates also originates from landfill materials.

Effluent standards were defined in February 1994. The permissible limit is 0.1 mg/L or below.

3. INVESTIGATIONS OF LEACHATES AT FINAL DISPOSAL SITES

In 2001, we selected 20 sites from among landfill sites for non-industrial waste in Japan and investigated the quality of leachates and their treated water. The general quality of water was investigated for the 6 substances mentioned above, as well as pH, SS, BOD, COD, etc.

The results of the investigations show that levels of nitrate nitrogen and nitrite nitrogen at some sites are high. These results may be due to the operational control of nitrification and nitrogen removal processes in biological treatment. Fluorine concentrations in leachates at most landfill sites are about 1mg/L. Although all boron concentrations of leachates are 10 mg/L or below, boron concentrations at some sites are higher than 2 mg/L, and concentrations of treated leachates are the same as those of raw leachates. Selenium concentrations at most landfill sites are below the minimum limit of determination. Figures 1-4 show the quality of water at each landfill site. Figures for antimony and selenium are omitted because their concentrations are very low.

4. SUPPLEMENTAL INVESTIGATIONS OF ACTUAL CONDITIONS

We focused on boron. It was reported that boron concentrations of leachates were 0.37 – 2.3 mg/L at final landfill sites for non-industrial waste where land-filling was in progress, and were 0.19 – 1.2 mg/L at sites where land-filling had been completed.²⁾ In 2002, we conducted supplemental investigations at 3 sites (J, K, and L) where concentrations of boron were higher than these values. Figures 5 - 7 show the results.

According to Figure 3 for the initial investigations and Figure 7 for the supplemental investigations, boron concentrations of raw leachates and those of treated leachates are almost same. This result suggests that boron cannot be removed by conventional water treatment methods.

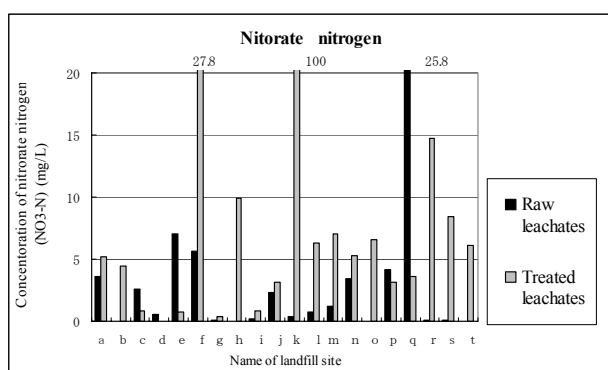


Figure 1. Concentration of nitrate nitrogen

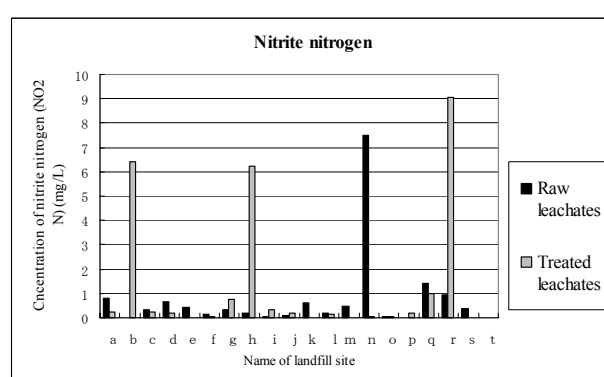


Figure 2. Concentration of nitrite nitrogen

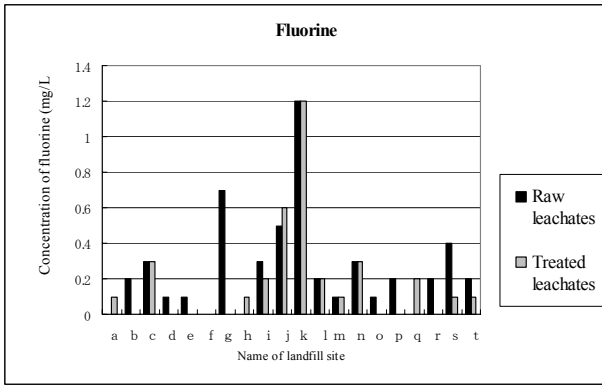


Figure 3. Concentration of fluorine

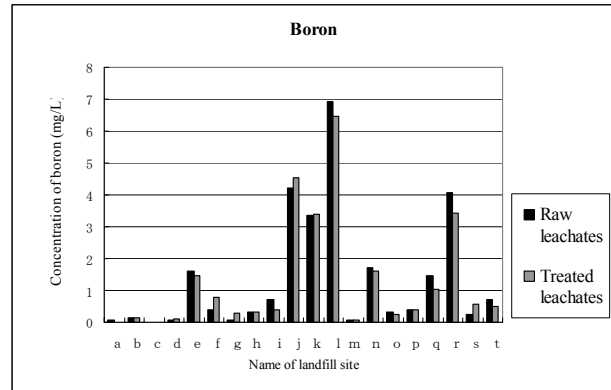


Figure 4. Concentration of boron

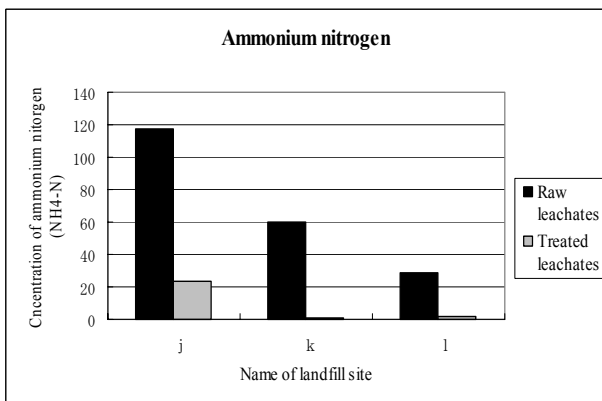


Figure 5. Ammonium nitrogen (supplemental investigation)

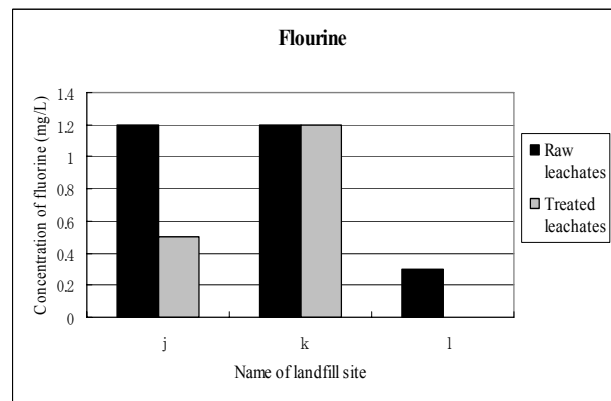


Figure 6. Concentration of fluorine (supplemental investigation)

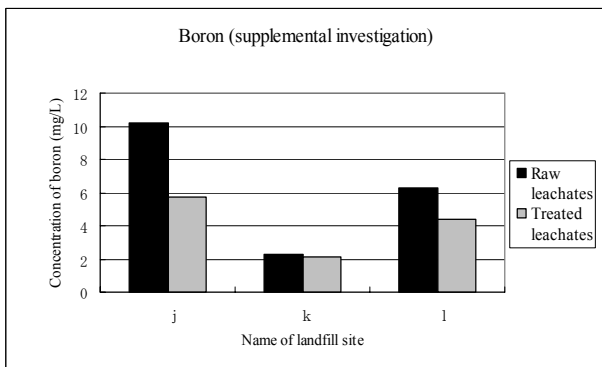


Figure 7. Concentration of boron (supplemental investigation)

5. BORON TREATMENT TECNOLOGY

As the investigation data show, it is difficult to treat boron using the traditional water treatment process. However, some treatment methods for boron are known and we explain the common ones.

For boron in water, the coagulation sedimentation method, the method of adsorption with

chelate resin, the solvent extraction method, and the reverse osmosis method (RO) are known treatment technologies. We recommend the method of adsorption with chelate resin to satisfy effluent standards and environmental limits.

Boron form in water is affected by pH. It is said that boron forms boric acid (H_3BO_3) in the low pH range and the hydrolyzed form ($B(OH)_4^-$) in the high pH range. It is also reported that boron takes a form in which boric acid is bound when the boric concentration is high.³⁾

Representative treatment methods such as the coagulation sedimentation method by which aluminum salt and calcium salt are added, the adsorption method with a chelate resin having the n-methylcurcumin radical which selects boron, and the solvent extraction method which applies an organic solvent of the hydroxyl group (-OH) are explained in the following sections. Each method has advantages and disadvantages. The appropriate method should be selected according to the wastewater conditions of the target.

5.1 The coagulating sedimentation method by adding calcium and aluminum salts

The principle of this method is as follows; boron is adsorbed by or reacts with calcium aluminate, which is generated when pH is adjusted in the range of 12 to 13 in the presence of calcium ion and aluminum ion. For wastewater containing a high concentration of boron, this method reduces the boron concentration to 1 mg/L. Table 4.1-1 shows the results of a study on eliminating boron by adding chemicals under various conditions. By adding 8400 mg/L of aluminum sulfate under pH 12.35, 50.6 mg/L of boron in raw water is reduced to 1.3 mg/L.³⁾

Because the amounts of chemicals used by this method and the amount of sludge generated as a result are very large, cost-reduction measures by combining the adsorption method or others should be considered. In addition, this method cannot process fluoroborate (combination form of boron and fluorine) ions.

Table 1. Result of coagulation sedimentation³⁾

Added chemicals	Boron concentrations of raw water (mg/L)	Amounts of added chemicals (mg/L)	Added amount of $Ca(OH)_2$ (mg/L)	pH (-)	Boron concentrations of treated water (mg/L)
PAC	58.5	8000	15000	12.65	44.6
Activated alumina	57.8	16000	15000	10.9	40.2
$AlCl_3 \cdot 6H_2O$	50.7	5790	15000	12.65	35.4
$MgSO_4 \cdot 7H_2O$	58.5	4000	15000	12.9	45.8
$FeSO_4 \cdot 7H_2O$	53.6	4000	15000	12.55	49.3
Na_2CO_3	58.5	4000	15000	12.9	43.4
$Al_2(SO_4)_3 \cdot 18H_2O$	50.6	1000	15000	12.5	40.6
$Al_2(SO_4)_3 \cdot 18H_2O$	50.6	5000	15000	12.45	13.6
$Al_2(SO_4)_3 \cdot 18H_2O$	50.6	5000	15000 (+ H_2SO_4)	7.4	34.5
$Al_2(SO_4)_3 \cdot 18H_2O$	50.6	8000	15000	12.35	1.3

NOTE: Raw water: H_3BO_3 + distilled water, reaction time: 30 min

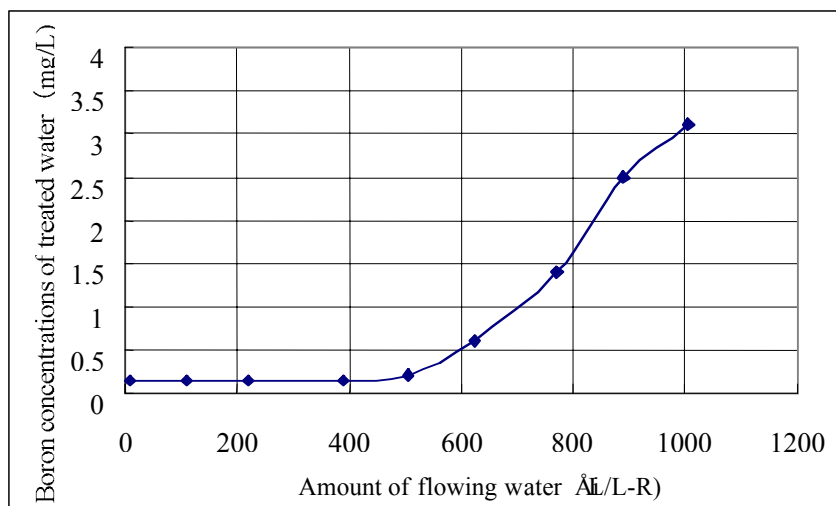


Figure 8. Flow examination result for boron adsorption resin ³⁾

5.2 The adsorption method

Boron is eliminated by flowing water containing boron through a resin having the n-methylcurcumin radical, which reacts selectively with boron (borate ion). Adsorbed boron is desorbed by acid. Resin is regenerated by alkali and can be used repeatedly. This method is aimed at the middle range of boron concentrations (around 100 mg/L) and is appropriate for reducing the boron concentration to 1 mg/L or below. Figure 4.1-1 shows one example of the flow examination result obtained by adsorption resin. 4.4 mg/L of boron concentration in raw water were reduced stably to 1 mg/L or below until the amount of running water reached about 700 times the amount of the resin. ³⁾ This method requires periodic resin exchange and handling/disposal of effluent for regenerating resin. To treat effluent generated to regenerate resin, the method whereby valuable elements are collected is proposed in combination with the solvent extraction method and the crystallization method. ³⁾

5.3 The solvent extraction method

To isolate boron using the solvent extraction method, wastewater containing boron is brought into contact with chemical agents; an agent that dissolves boron physically, an agent that generates neutral ester by reacting with boron, and an agent that forms a complex with boron (mainly organic solvent such as higher alcohol or diol) were examined for application with this method.

This method was studied for applications to isolate boron from ore containing boron and to regenerate boron adsorption resin. Figure 9 is a flow chart of the sodium borate (used as glass raw material) recovery system in which boron adsorption resin, solvent extraction method, and crystallization method are combined. Using this system, sodium borate can be used effectively and waste is not generated. ³⁾

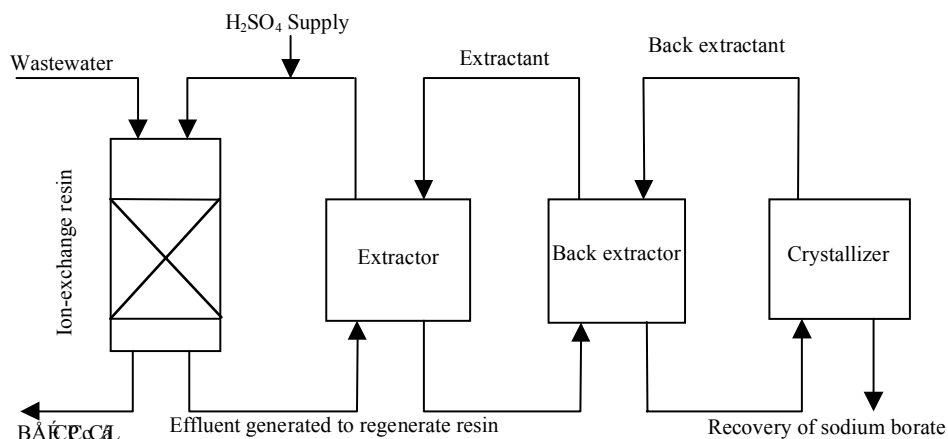


Figure 9. Boron recovery flow chart ³⁾

Because most boron extraction agents have a hydroxyl radical (OH), they are hydrophilic and dissolve in water. Therefore, some kinds of agent may increase BOD and COD in wastewater. In addition, safety issues related to malodors and flammability should be considered. ³⁾

6. BORON TREATMENT TESTS

We performed boron treatment tests. The resin adsorption method was selected from among the available treatment methods, and the test was performed on treated leachates at the K and L disposal sites.

Table 2. Fluid volume and boron concentrations of treated leachates

K landfill site		L landfill site	
Concentrations of raw leachates	2.5mg/L	Concentrations of raw leachates	4.9mg/L
Fluid volume (L/L-R)	Boron concentration (mg/L)	Fluid volume (L/L-R)	Boron concentration (mg/L)
50	<0.1	43	<0.1
251	<0.1	244	<0.1
401	<0.1	398	<0.1
501	<0.1	552	0.3
602	<0.1	655	4.4
702	<0.1	758	4.9
802	<0.1	861	5.2
902	<0.1	912	5.5
1003	<0.1	-	-

[Note 1] SV: flow rate per unit of time / filler volume (SV = 5H⁻¹ means 150 mL/H of flow rate)

[Note 2] Fluid volume L/L-R: fluid volume against apparent volume of filler

Table 3. Content analysis and leaching test of landfill materials and cover soil (L landfill site)

Test	unit	Cover soil	Landfill materials	
Leaching test	Pb	(mg/L)	0.01	0.17
	B	(mg/L)	<0.02	0.22
	F	(mg/L)	0.3	0.8
Content analysis	Pb	(mg/kg)	15	437
	B	(mg/kg)	1	67
	F	(mg/kg)	54	30
	Percentage of water content	(%)	17.2	13.8

We filled a 7-mm-dia column with 30 ml of adsorption resin for boron and passed sample fluids through the column under $SV = 5H^{-1}$. For the sample at the K disposal site, boron did not leak until the fluid volume reached 1003 L/L-R. For the sample at the L disposal site, boron began to leak when the fluid volume reached about 550L/L-R. Boron adsorbed by chelate resin was above 2.51 g/L-R for the K disposal site and 2.94 g/L-R for the L disposal site. Table 1 shows the results.

7. BORON LEACHING TEST FOR LANDFILL MATERIALS AND COVER SOIL

It is reported that boron in leachates at landfill sites for non-industrial waste is attributed to non-combustible waste. ²⁾ We investigated cover soil to study other factors.

To determine boron sources in the L landfill site, we obtained landfill materials (mainly noncombustible waste) and cover soil. We measured their boron content, and performed a leaching test. The leaching test was performed as per public notification No. 13 of the Environment Agency of Japan. Table 2 shows the results. These results suggest that boron in leachates at the L landfill site originates from landfill materials.

6. SUMMARY

The sectional committee has focused on and investigated non-regulated substances in leachates at final landfill sites. We planned the investigation in the first year and performed it in the second year. As mentioned above, the concentrations of the 6 non-regulated substances we investigated are low. However, when the boron concentration in raw leachates is compared to that in treated leachates, they are almost the same. This result suggests that conventional treatment methods do not work well in a boron treatment process. In addition, the data for nitrate nitrogen and nitrite nitrogen at some sites suggest that nitrogen removal in the water treatment process is not effective.

New effluent standards for nitrogen, fluorine, and boron were established during our studies, and these elements became regulated. Treated leachates at any sites are within permissible limits according to the new standards. However, some local governments define local effluent standards for boron more stringently than the national standards. We paid attention to leachates whose boron concentrations are higher than such local standards, and performed supplemental investigations.

The results of supplemental investigations are much the same as the results of the first investigations. We obtained leachates at some sites where boron concentrations are higher than

the local standards, 2 mg/L, and performed the treatment test. The results of treatment were satisfactory. In addition, we performed leaching tests and content analyses for landfill materials and cover soil at the sites. The results suggest that the boron source is not cover soil, but landfill materials.

With the exception of nitrogen, the concentrations of the 6 substances we investigated raise no problems, but at some sites, boron originating from landfill materials is controversial. If the boron concentration becomes a problem, the chelate adsorption method can be applied.

The investigations were conducted by the sectional committee for the water environment of the Landfill Systems & Technologies Research Association of Japan.

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