Development of an Ion Removal Technique Based on Capacitive Deionization for Treatment of Rinse Water from Incineration Ash

Ginno Lizano ANDRES*, Nobuyuki YANO*, Yuuki SHIYOUKEI*, Yoshinobu YOSHIHARA*, Masakazu TANAHASHI**

*Mechanical Engineering Department, Ritsumeikan University, 1-1-1 Noji-higashi, Kusatsu, Shiga 525-8577, Japan
**Tanah Process LTD., 4-2-7-204 Shimaya Konohama-ku, Osaka-shi, Osaka 554-0024, Japan

ABSTRACT
Capacitive deionization technique having higher efficiency and lower operation cost in comparison with the reverse osmosis technique for regeneration of rinse water used for dechlorination of incineration ashes is investigated. Activated charcoal-based electrodes were developed and characterized for their capacity to remove the chlorine ions dissolved in rinse water for incineration ashes. The mass ratio of rinse water to incineration ashes was also investigated to realize the most efficient removal of chloride from rinse water and minimize the regeneration load of the rinse water. The electrochemical properties of the developed electrode were characterized using a three-electrode cyclic voltammetry system, which showed that chemically modified carbon electrodes demonstrated an increase in capacitance. An asymmetrical distribution of capacities of both electrodes was found to be ideal wherein no electrochemical reactions took place at the electrode surface. The electrode capacities were defined based on the difference between the rest potential of the electrodes and the oxidation-reduction potential of the solution. Furthermore, the ion removal capacity of the electrode was evaluated using NaCl solution with a conductivity of 11 mS/cm. The electrode with a thickness ratio of 2.5:1 (anode:cathode) exhibited high ion removal capacity up to 0.034 mol/m².

Keywords: activated charcoal electrode, bottom ash, capacitive deionization

INTRODUCTION
In Japan, 50 million tons of municipal solid wastes (MSW) are generated per year and those wastes are incinerated to maintain sanitation and to reduce those volume and mass. The mass reduction in incineration is about 90% while 10% of residual incineration ashes have been buried in landfills. However, landfills for incineration ashes are becoming difficult and problematic due to high cost, environmental issues, lack of available land and strict laws. At present, in some municipal waste treatment plants in Japan, incineration ashes are melted to make a molten slag to promote recycling as construction materials or aggregates. The energy cost to heat up to around 1,700 K is preventing it in becoming popular. The molten slag also has the problem in strength as the aggregate materials. Another way to promote recycling is to use the incineration ash as a raw material for concrete manufacturing. Since the chemical composition of incineration ashes is similar to cement, the quantity going into landfills can be reduced. However, incineration ashes usually have high chloride ion content, which causes metal erosion especially in reinforced concrete. Therefore, the amount of incinerated ashes accepted is limited by the high cost and huge consumption of energy of the chlorine bypass system typically used for controlling the chloride content of the incinerated ashes. An alternative method to remove chloride is by washing the incineration ashes.
with water. This method requires large quantities of water for rinsing which must then be treated for reuse. Reverse osmosis (RO) is the most popular water treatment technology for this purpose. However, RO requires the pretreatment of its membrane to prevent clogging by the sludge in the liquid. The process also uses a large quantity of energy and the high cost of the fabrication as well as the maintenance can be prohibitive. The capacitive deionization (CDI) technique could be used as an alternative to other water treatment technologies (Welgemoed and Shutte, 2005). Capacitive Deionization is a potential induced system in which a positively and negatively charged electrode adsorbs negative and positive ions, respectively. The adsorption of ions at the electrode surface utilizes the principle of electric double layer theory (Farmer et al., 1995), wherein the ions from the ionic liquid are adsorbed due to coulombic interaction rather than electrochemical reaction (Oh et al., 2006). Once the electrode reaches its maximum adsorption capacity and the electrode pores are saturated with ions, the adsorbed ions can be easily regenerated by simply reversing the applied current or short-circuiting the parallel electrodes. One of the key advantages in CDI is that the stored energy at the electrodes that are electrically charged can be reused for another process in an optimized energy recovery system. Anderson et al. (2010) postulated that if an efficiency of over 85% can be attained for CDI, it could become a serious competitor to reverse osmosis, not only for brackish water but also for seawater desalination. Additionally, CDI is environmentally friendly because there is no need to use chemicals during regeneration. This technique is a simple and nearly maintenance-free system. Furthermore, by utilizing the energy recovery system, the running cost in CDI is more cost-effective than RO. In fact, the energy needed to desalinate seawater in RO is 3.5 to 2.5 kWh/m³ with < 30 to 40% water recovery, whereas in CDI with > 80 to 90% water and energy recovery, would require only 2 to 1 kWh/m³. Thus, CDI is three times more economical than RO for the treatment of 1 million gallons per day of brackish water (Welgemoed and Schutte, 2005).

Many researches concerning the use of CDI technique for water purification have been reported, particularly for the development of electrode with novel materials that have high electrical conductivity and high ion removal capacity. Carbon aerogel is one of the promising materials for CDI due to its high electrical conductivity and low electrical resistance of less than 40 mΩ·cm (Park et al., 2011). Recently, researchers focused on enhancing the ion removal capacity of the carbon electrode by incorporating ion-exchange membrane and electrode-coated ion-exchange polymer (Biesheuvel and Wal, 2010; Kim and Choi, 2010). Others focused on the CDI operation optimization such as investigation of adsorption/desorption mechanisms of carbon electrode and electrode reactions (Lee et al., 2010). Comparison of mono and bipolar connections in CDI operation for the treatment of NaCl has been reported (Lee et al., 2012).

Even though the aforementioned carbon materials exhibited excellent physical and electrochemical properties with high ion removal performance for CDI application, these electrodes still suffer from their relatively complicated fabrication process. This results to a high cost of electrode material, thus limits its commercial application. Choi (2010) has developed a relatively low-cost activated carbon powder-based electrode which composed of carbon powder and a polyvinylidenefluoride (PVDF) solution as a polymeric binder. The developed electrode exhibited good electrochemical property and ion removal capacity. Because of the remarkable efforts done and following the method
of Choi (2010) for electrode fabrication, Nadakatti et al. (2011) and Hou et al. (2012) conducted investigations that were aimed to enhance the electrosorption ability by incorporating mesoporous carbon black (MCCB) and by morphological structure modification by chemical treatment, respectively.

In this study, carbon electrodes made of activated charcoal powder, polymeric binder and conductive material was developed. Activated charcoal powder (ACP) is known to be economical and yet effective as electrode material with specific surface area > 2,000 m²/g. Conductive carbon black was incorporated to enhance the ion adsorption capacity of the fabricated electrode. Studies on the use of conductive carbon black to harness the ion adsorption capacity are limited (Park et al., 2007 and Nadakatti et al., 2011). Furthermore, a simple screen printing method was employed to produce the electrodes. Moreover, the structure of the developed electrode was modified using alkaline electrolyzed water. The developed carbon electrode was characterized by its ion removal capacity, particularly for ions dominant in wastewater from incineration ashes. The electrochemical behavior of the prepared electrodes was evaluated by a three-electrode cyclic voltammetry (CV) system. The carbon electrode’s charging and discharging behaviors and electrode reactions were also investigated. To evaluate the potential use of the electrode for dechlorinating wastewater, the mass proportionality ratio of the rinse water to incineration ashes was investigated to determine the optimum mass ratio for the removal of chlorine ions.

MATERIALS AND METHODS
Fabrication of polymeric-based activated charcoal electrodes
The carbon electrodes were fabricated by mixing activated charcoal powder (ACP, Dainen Corp., Japan, specific surface area = 1,964 m²/g), conductive carbon black (CCB, Nippon Graphite Industries Ltd., Japan, SP-270, average particle size = 4 μm, BET surface area = 250 m²/g), polyvinylidene difluoride (PVDF, Kureha Corp., Japan, W#1100) and N-methyl-2-pyrrolidone (NMP, Nacalai Tesque, Inc., Japan, 99.5%). PVDF and NMP were used as the polymeric binder and organic solvent, respectively. The screen printing technique was performed by directly pouring the slurry on a screen to form a solid activated charcoal electrode. These electrodes were dried at room temperature for 24 h, followed by subsequent drying for 2 h each at 50°C in a constant temperature oven and vacuum oven, respectively, to evaporate all organic solvents in the electrode pores. The thickness of the dried electrode was then measured. The microstructure of the carbon electrode was modified by soaking it in alkaline electrolyzed water (pH 12) (Tanah Process Ltd., Japan) for 24 h, after which it was washed by deionized water several times.

Several electrode compositions were tried and evaluated using different polymeric binders such as PTFE, PVB, SBR, and PVDF. In this experiment, PVDF shows better binding property particularly when the electrode was attached at the graphite sheet current collector. Also, various ACP:CCB:PVDF compositions were used. Of all compositions tried, 15% PVDF exhibited high ion removal efficiency and high mechanical strength. Details of the experiment are described elsewhere (Andres et al., 2013a, b). Thus, after a series of electrode fabrication it was found that the optimum composition of the electrode was 75% ACP: 10% CCB: 15% PVDF mainly due to its
high mechanical stability. The efficiency of the fabricated electrodes was evaluated using a manufactured single unit cell capacitive deionizer.

**Fabrication of CDI cell**
The CDI single cell was composed of (a) fabricated carbon electrodes, (b) graphite sheets where the carbon electrodes were attached to act as a current collector, (c) a 58-μm thick PET net separator inserted between the two electrodes as the non-conductive separator to prevent short circuits and used as a pathway of the flowing electrolyte, and (d) a PET spacer with a thickness of 1 mm to maintain the distance between the pair of electrodes.

**Physical and electrochemical properties of the developed electrodes**
The physical microstructure of the prepared activated charcoal electrodes was observed by scanning electron microscopy (SEM) (Keyence, Japan). The morphological microstructures of the electrode were evaluated by Brunauer-Emmet-Teller (BET) under nitrogen adsorption/desorption at –196°C, and were performed using Autosorb 1 (Quantachrome Corp., USA) analyzer. The electrochemical properties of the fabricated carbon electrodes were characterized by three-electrode CV measurements using a potentiostat (HAL 3001, Hokuto Denco, Japan) at 5 mV/s potential sweep rate in 3.5% NaCl at 25°C. A silver/silver chloride (Ag/AgCl) saturated KCl electrode was used as a reference electrode. By keeping the potential sweep rate $1/(dV/dt)$ constant, the capacitance $C$ can be directly calculated as follows:

$$ C = \int i \frac{dt}{dV} $$

where $i$ is the current, $t$ is the time, and $V$ is the voltage.

The charge and discharge behaviors of the fabricated electrodes were determined by connecting the galvanostatic charge/discharge instrument to the potentiostat. The charge and discharge were kept constant at 100 mA while the potentiostat recorded the charge/discharge data from the anode. The effective area of the paired electrodes was 81 cm$^2$.

**Ion removal performance of the prepared activated charcoal electrodes**
To examine the capacitive deionization performance of the developed electrodes, Na and Cl removal capacity measurements were carried out by manufacturing a CDI single cell. The CDI evaluation was conducted by charging a pair of electrode up to 1.2 V to avoid the electrolysis of water. The charging and discharging current was limited to 100 mA DC supply using a galvanostatic charge/discharge instrument. During the charging process, the electrode’s potential was held constant after reaching its set maximum voltage. A 20 mL of charge processed and another 20 mL for regeneration process solution were collected. The processed solutions were thoroughly mixed before measuring the conductivity using ion conductivity meter (Laqua F-74, HORIBA, Japan). The initial conductivity of the prepared NaCl solution was 11 mS/cm or 0.11 mol/L concentration. Capacitive deionization measurements were executed under batch conditions.
Preparation of extracted ash sample (soluble and non-soluble chloride measurements)

The incineration bottom ash sample was supplied by one of the incineration plants in Kyoto, Japan. The sample was dried in a constant temperature oven for several hours to evaporate the moisture from the ash. It was then crushed into small particles and all metals were removed using a magnet. The desired amount of the prepared ash was washed with water. The ash and water were mixed vigorously for 1 h before separating the washed ash from the water using porous filter paper (5A, Advantec, ø = 300 mm). The water solution was analyzed by a Cl electrode (Horiba, Japan) to measure the amount of soluble chloride. The washed ash was dried for 12 h at 105°C, then placed into a PTFE cylinder and washed again with pure water and HNO₃ solution. The dilution liquid was prepared in a ratio of 1:1 (HNO₃:pure water). Nitric acid was used to dissolve the non-soluble chloride after which it was placed on a hot plate and heated for 1 h at 130°C. It was then cooled at room temperature for 12 h before filtering and placed directly into a 250 mL container. Finally, the solution was analyzed by a Cl electrode to measure the amount of non-soluble chloride (Japan Standards Association, 2010, 2012).

Preparation of extracted ash samples for alkali metal, alkali earth metal, and heavy metal ions analysis

The elemental concentrations of extracted incineration ash particularly heavy metal ions were analyzed using inductively coupled plasma atomic emission spectrometer (ICP-9000, Shimadzu, Japan). Ash samples were prepared at given mass ratios of rinse water to incineration ash. After washing, the mixture was carefully filtered using porous filter paper to separate the solid from the liquid. Because the concentration of ions from the solution varied, different dilution ratios using the prepared dilution liquid (HNO₃: pure water = 1:500) were used for accuracy of the measurements. The pH of the solution was maintained at < 2 to prevent scaling at the nano-sized nozzle of the ICP instrument (Japan Standards Association, 2010).

RESULTS AND DISCUSSION

Physical and electrochemical property characterization of the prepared activated charcoal electrodes

This is the first time that screen printing technique was employed in manufacturing electrode for capacitive deionization. Table 1 shows the novelty of the electrode fabricated with previous studies. Figures 1a and 1b show the SEM micrograph of the electrode surface and cross-sectional view, respectively. As shown in the figure, the electrode is permanently attached at the graphite sheet or current collector, and the ACP is effectively bound together with agglomerated small and large pore sizes thus formed a uniform electrode layer. In fact, when the electrodes were rubbed by hand, the ACP did not fall off. Also, when the electrodes were placed in flowing water, the ACP easily got wet and remained intact. To assess the wettability of the developed electrode, approximately 0.5 mL of water was dropped on the electrode surface layer. As shown in Fig. 1c to 1f, the water droplet on the electrode changes its contact angle by the time it was dropped, thus, it was immediately absorbed after 4 s. This indicates high wettability of the electrode.
Table 1 - Comparison of the electrode composition and physical characteristics from previous works.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Park et al. (2007)</th>
<th>Nadakatti et al. (2011)</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>84:12:4</td>
<td>70:10:20</td>
<td>75:10:15</td>
</tr>
<tr>
<td>Solvent</td>
<td>isopropyl alcohol</td>
<td>ultrapure water</td>
<td>NMP</td>
</tr>
<tr>
<td>Method</td>
<td>roll press</td>
<td>mold and compression</td>
<td>screen print</td>
</tr>
<tr>
<td>Anode thickness [μm]</td>
<td>300</td>
<td>70 – 550</td>
<td>220</td>
</tr>
<tr>
<td>Cathode thickness [μm]</td>
<td>300</td>
<td>220</td>
<td></td>
</tr>
</tbody>
</table>


Fig. 1 - SEM (230 × magnification) micrographs of developed electrode (a) surface and (b) cross-sectional view. Contact angle images of a drop of water on the electrode at different time (c) 1s, (d) 2s, (e) 3s, (f) 4s.
It is known that carbon functional group such as carboxyl, carbonyl, and hydroxyl groups enhance the hydrophilic property of the electrode (Seo et al., 2010). The contact angle observation and SEM micrographs validate that the fabricated electrode poses strong hydrophilic property as well as high mechanical strength. In CDI system, electrode with high wettability rate is ideal because it affects the total effective areas for ion accommodation and ion removal capacity during capacitive deionization process.

The electrochemical properties of the prepared carbon electrodes were evaluated by cyclic voltammetry and charging/discharging behavior. In these experiments, a carbon electrode 220 µm thick was used as the auxiliary electrode to carry out the cyclic voltammetry measurements. As shown in Fig. 2, the capacities of the electrodes in potential windows from 0.2 V to 0.6 V varied with increasing working electrode thickness. The capacitances of the carbon electrodes were as follows: 12 F, 28 F, 46 F, 57 F, and 88 F for carbon electrodes with thicknesses of 70 µm, 150 µm, 250 µm, 290 µm, and 550 µm, respectively. Since the rest potential (RP) of the fabricated carbon electrodes was around 0.14 V – 0.2 V, the CV measurement started from 0.2 V. The results demonstrate that as the thickness increases, the capacitance also increases. Higher capacitance could indicate better electroosorption performance. In this evaluation, cyclic voltammograms show nearly rectangular shape which indicates that ions were adsorbed in a form of electrical double layer without chemical reactions within electrode/solution interfaces. Nevertheless, CV of 550 µm thick electrode illustrated a rectangular shape with a little deviation, mainly due to the slow transient of ions into the high resistance micropores.

Figure 3 shows the oxidation/reduction potential of water solution against the Ag/AgCl standard electrode potential and the standard hydrogen electrode (SHE) potential, wherein the electrolysis of water takes place under a 1.23 V or more electrode gap. As mentioned above, the rest potential of the fabricated carbon electrodes was around 0.14 V – 0.2 V, therefore, the anode has only a 0.42 V – 0.48 V margin in potential against the oxidation. On the other hand, the cathode has a 0.75 V – 0.8 V margin against the reduction. If the same electrode is used having the same capacities for anode and cathode, oxidation takes place at around 0.84 V – 0.96 V (0.42 V – 0.48 V × 2), which results in a voltage loss wherein the potential gap up to the electrolysis of water (1.23V) is not fully utilized for ion capturing. To compensate for this asymmetrical potential gap at anode and cathode, a pair of carbon electrodes with different capacities or different thicknesses would be more effective for capacitive deionization.
The charging and discharging behavior of the fabricated electrodes was studied in 0.11 mol/L NaCl solution and were performed using a potentiostat and galvanostatic charge/discharge instrument. As presented in Fig. 4a, in the case of a 1.1 thickness ratio of anode and cathode ($\delta_{\text{anode}}/\delta_{\text{cathode}}$), the charging potential of the anode exceeds the oxidation potential. Thus, oxidation takes place at the anode and the ion adsorption capacity is limited. On the other hand, for $\delta_{\text{anode}}/\delta_{\text{cathode}} = 2.5$ (Fig. 4b), neither the anode nor the cathode potentials exceeded the oxidation/reduction potentials. This indicates that electrochemical reaction or electrolysis of water did not take place. Therefore, $\delta_{\text{anode}}/\delta_{\text{cathode}} = 2.5$ is an ideal pair for effective capacitive deionization. Different anode:cathode ratios were examined and the results are summarized in Table 2.
Ion removal performance of the developed activated charcoal electrodes

The capacitive deionization performance evaluations were conducted using the manufactured capacitive deionizer comprising a pair of the developed carbon electrodes (anode and cathode) and the experimental process was described above.

Figure 5 shows the charging behavior of the fabricated electrodes with different asymmetrical capacities during the ion adsorption process. Ideal electrodes for CDI should have both high surface area and longer charging time. Longer charging time would indicate high effective surface area and more efficient ion adsorption. The charging time of the carbon electrode with $\delta_{\text{anode}}/\delta_{\text{cathode}} = 2.5$ is clearly longer than that of the carbon electrodes with $\delta_{\text{anode}}/\delta_{\text{cathode}} = 1.1$ and 0.7. This implies that ion adsorption of the electrode with 2.5:1 thickness ratio is higher. Thus, the trend in electric charge (Coulomb, C) for these asymmetrically paired carbon electrodes with $\delta_{\text{anode}}/\delta_{\text{cathode}} = 2.5$, 1.1 and 0.7 are 40 C, 31 C and 22 C, respectively.

Figure 6 shows a summary of the capacitive deionization performance evaluations. As expected, the electrode pair with the $\delta_{\text{anode}}/\delta_{\text{cathode}} = 2.5$ thickness ratio exhibited the highest ion adsorption capacity. From the initial conductivity (11 mS/cm), $\delta_{\text{anode}}/\delta_{\text{cathode}} = 2.5$, 1.1 and 0.7 were reduced to 9.73 mS/cm (0.034 mol/m$^2$), 9.97 mS/cm (0.026 mol/m$^2$) and 10.57 mS/cm (0.011 mol/m$^2$), respectively, after repetitive charge and

---

**Table 2 - Summary of charge/discharge behavior evaluation.**

<table>
<thead>
<tr>
<th>Anode:Cathode ratio</th>
<th>Anode potential [V]</th>
<th>Cathode potential [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3:1 (70:220 [μm])</td>
<td>0.94</td>
<td>-0.25</td>
</tr>
<tr>
<td>0.7:1 (150:220 [μm])</td>
<td>0.84</td>
<td>-0.29</td>
</tr>
<tr>
<td>1.1:1 (250:220 [μm])</td>
<td>0.77</td>
<td>-0.42</td>
</tr>
<tr>
<td>1.3:1 (290:220 [μm])</td>
<td>0.73</td>
<td>-0.46</td>
</tr>
<tr>
<td>2.5:1 (550:220 [μm])</td>
<td>0.58</td>
<td>-0.62</td>
</tr>
</tbody>
</table>

---
discharge processes. The change in ion conductivity indicates the adsorption and desorption of ions at the electrode’s pores. The ion removal capacity of the alkali-treated carbon electrode (soaked in alkaline electrolyzed water) was also analyzed. The $\delta_{\text{anode}}/\delta_{\text{cathode}}$ thickness ratio of electrode was 0.6 while indicated an ion removal capacity of 0.022 mol/m². Hence, it is relatively higher in comparison with $\delta_{\text{anode}}/\delta_{\text{cathode}} = 0.7$ thickness ratio. This result suggests that it is possible to increase the ion removal efficiency of the developed electrode by microstructure modification. The details will be discussed in the next section.

For further understanding regarding the developed electrode’s microstructure, BET surface area was examined. As shown in Fig. 7, the surface area of the carbon electrode increases along with increasing electrode thickness. The same trend was observed in ion removal capacity evaluation (Fig. 6) wherein the ion removal capacity is strongly related with the electrode surface area and the electrode thickness. On the other hand, alkali-treated carbon electrode (PVDF 140 $\mu$m) illustrated higher surface area even though it is thinner in comparison with the electrode having 150 $\mu$m thickness. This result agrees well with its ion removal performance.

---

**Fig. 5 - Charging evaluation of various electrodes with asymmetrical capacities at 0.11 mol/L NaCl aqueous electrolyte.**
Fig. 6 - Capacitive deionization measurements of the carbon electrodes with various thickness ratios at 0.11 mol/L (11 mS/cm) NaCl aqueous electrolyte.

Fig. 7 - Surface area of carbon electrode per unit mass of electrode including current collector with respect to electrode thickness.

Comparison of non-treated and chemically modified carbon electrode microstructures

As illustrated in Fig. 8, the electrochemical behaviors of non-treated and alkali-treated carbon electrodes were evaluated. The capacitance was calculated from the electrode rest potential to its peak current. The CV analysis was conducted at the potential range of −0.6 V to 0.6 V with a scan speed of 10 mV/s at 3.5% NaCl solution.
Choi and Choi (2010) reported that the capacitance of carbon electrode can be slightly decreased as the amount of PVDF binder increases. This is because the PVDF polymeric binder is hydrophobic and could decrease the accessibility of the transient ions at the electrode pores. On the other hand, polymeric binder can be useful in preventing redox reaction at the surface of the electrode. To overcome the problem mentioned, the electrode was treated with alkaline electrolyzed water. Previous works have modified their electrodes using strong base such as potassium hydroxide (KOH) (Park et al., 2007). The capacitance increased after soaking the electrode into an alkaline electrolyzed water in which OH\(^-\) ions are abundant. The rest potential of the carbon electrode was changed after alkali treatment from 0.17 V to 0.018 V where the capacitance was increased up to 1.7 times. Moreover, as shown in Fig. 8, the cyclic voltammogram of the non-treated carbon electrode exhibited a slight distortion within negative potentials, which is assumed to be related to pseudo-Faradaic reaction between electrode/solution interfaces. In contrast, weak pseudo-capacitance was not observed in cyclic voltammogram of the alkali-treated electrode not only at the same potential range but also at lower potential. This implies that some hydrophobic area of the carbon electrode was transformed into a more hydrophilic, mainly because of the effect of -OH functional groups. Although the BET surface area analysis of alkali-treated electrode exhibited a slight improvement as can be seen in Fig. 7, its ion removal capacity was increased significantly. This indicates that since the hydrophilicity of the developed carbon electrode was enhanced by alkaline treatment, its effective surface area was also increased. In principle, even though the surface area of the carbon electrode is high but if the liquid could not access through the carbon electrode meso and micro pores, high surface area is insignificant.

To further examine the electrode transformation phenomenon, ion-removal performance of the non-treated and alkali-treated carbon electrode has been evaluated. In the case of
the non-treated electrode, from 450 μS/cm NaCl solution conductivity, it was reduced to an average conductivity of 190 μS/cm. The ion removal efficiency was 57%. On the other hand, treated carbon electrode exhibited an ion removal efficiency of 81% (from 407 μS/cm to 90 μS/cm). The result from ion removal evaluation is in good agreement with the cyclic voltammetry measurement. The ion removal efficiency, electrode capacity, and effective surface area of alkali-treated carbon electrode were higher than those of the non-treated carbon electrode. These results indicate that the property of the carbon electrode could transform from some hydrophobic surface area to a more hydrophilic property using alkaline electrolyzed water. This leads to increased ion removal efficiency.

**Analysis of soluble and non-soluble chloride**

To evaluate the required specification of the CDI system for the treatment of rinse water from incineration ash, the behavior of chloride in rinse water has been observed. The mass ratio of rinse water to incineration ashes was investigated to realize the most efficient removal of chloride from rinse water and minimize the regeneration load of the rinse water. It is said that approximately 1 – 2% of chloride is included in an incineration bottom ash. In addition, the chlorinity is known to change by difference in incinerator type and in quality of garbage by the season. The chloride content of the bottom ash of the stoker type incinerator, with a rating capacity of 400 t/day in spring, was measured and analyzed. In this evaluation, it shows that the total amount of chloride in the ash sample was 1%. Figure 9 shows the removal efficiency of the mass ratio of rinse water to bottom ash. The moisture content after washing was found to be 35%. Chloride removal efficiency with respect to the mass ratio was calculated using equation 2

\[ R_r = a \left(1 - \frac{m_w}{x}\right) \times 100 \]  

(2)

![Figure 9 - Mass ratio of rinse water to bottom ash.](image-url)
where, $a$ is the soluble Cl ratio to total Cl, $m_w$ is the moisture content after washing, and $x$ is the mass ratio of rinse water to dry ash. Measuring the moisture content of the ash after washing plays an essential role particularly when analyzing the soluble chloride. It could cause serious problems when used as aggregate for concrete manufacturing. In the case of ratio to soluble chloride, the removal rate was calculated to be 91% for a solid:liquid ratio of 1:4. Whereas the chloride contents in extracted bottom ash, for soluble and non-soluble chloride are 75% and 25%, respectively. Non-soluble chloride is believed to exist together with other compounds such as calcium oxide (CaO) and aluminum oxide (Al$_2$O$_3$) or Friedel’s salt. Utilizing equation 2, the calculated removal rate for a solid:liquid ratios of 1:2, 1:4 and 1:6 are 62.2%, 68.8% and 70%, respectively. The chloride removal efficiency of the experimental data was measured to be most likely identical to the calculated one as shown in Fig. 9. This specifies that soluble chloride was dissolved perfectly while the residual chloride with rinsed ash is non-soluble chloride and soluble chloride exists in the residual water in ash. Meanwhile, as rinse water increases the rate of soluble chloride increases, which implies that almost all chloride was dissolved. Furthermore, within the range of 1:3 and 1:4 mass ratio of rinse water to bottom ash appears to be both ideal for effective analysis and economical for brackish water purification. This result signifies that the analysis is accurate when soluble and non-soluble chloride exist in the extracted bottom ash sample.

Elemental concentration analysis of extracted bottom ash samples

Heavy metal concentrations in incinerated ash vary depending on volatility and boiler combustion conditions during the incineration process. Bottom ash usually does not need to be treated due to its low heavy metal concentrations. However, there are standards that must be considered since heavy metals from incineration ash could cause negative effects on the environment and especially on human health. Therefore, it is highly critical to determine the concentration of heavy metals in incineration ash and control their amounts. Bottom ash samples A, B and C were obtained from stoker type incineration plants having different rating capacities such as 400 t/day, 600 t/day and 700 t/day, respectively. Table 3 presents the analysis of extracted bottom ash samples, A, B and C, with a 1:4 mass ratio of rinse water to bottom ash. The pH values of all ash samples indicate high alkalinity when alkali metals such as Na and K are abundant. Alkaline earth metal Ca is present in significant amounts with an average concentration of 156 mg/L whereas the Mg average content varies. Heavy metal ions are present in a minimal amount except for Pb and Cu with concentrations ranging from 0.2 – 0.6 mg/L and 0.1 – 0.6 mg/L, respectively.

Table 3 - Elemental analysis of the bottom ash with 1:4 mass ratio of ash to rinse water.

<table>
<thead>
<tr>
<th>Element</th>
<th>Bottom ash A</th>
<th>Bottom ash B</th>
<th>Bottom ash C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0.13</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Ca</td>
<td>229</td>
<td>167</td>
<td>71</td>
</tr>
<tr>
<td>Cd</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>0.11</td>
<td>0.06</td>
<td>0.17</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>K</td>
<td>538</td>
<td>393</td>
<td>303</td>
</tr>
<tr>
<td>Li</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Mg</td>
<td>0.02</td>
<td>0.166</td>
<td>0.004</td>
</tr>
<tr>
<td>Mn</td>
<td>0.004</td>
<td>0.008</td>
<td>0.002</td>
</tr>
<tr>
<td>Na</td>
<td>460</td>
<td>412</td>
<td>917</td>
</tr>
<tr>
<td>Pb</td>
<td>0.5</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Sr</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>0.02</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>pH</td>
<td>10.3</td>
<td>10.1</td>
<td>11.8</td>
</tr>
<tr>
<td>Cl</td>
<td>1,787</td>
<td>1,078</td>
<td>1,350</td>
</tr>
<tr>
<td>DS</td>
<td>3,380</td>
<td>3,810</td>
<td>3,650</td>
</tr>
</tbody>
</table>

Unit : mg/L

DS: Dissolved solids
CONCLUSIONS
Activated charcoal-based carbon electrodes were fabricated and evaluated. The developed carbon electrodes possessed high hydrophilic properties and high mechanical strength. For effective capacitive deionization, an asymmetrically paired capacity carbon electrode was determined to be ideal. Consequently, electrochemical reaction between the electrodes and the electrolyte interface was prevented, effectively utilizing the supplied potential. For the developed electrodes, a suitable $\delta_{\text{anode}}/\delta_{\text{cathode}}$ was 2.5. The hydrophilic property of the carbon electrode was enhanced by chemical modification.

The proportionality ratio of rinse water to incineration bottom ash was evaluated. Although there were several other ions present in the bottom ash, sodium and chlorine ions were abundant. The analysis suggests that the CDI system fabricated can be used to treat incinerator ash wastewater.

ACKNOWLEDGEMENTS
This work was financially supported by the Ministry of Environment of Japan under Grant No. K122012. The authors would like to acknowledge Dainen Corporation for providing the activated charcoal powder and Tanah Process LTD for introducing the batch condition experiment and for providing assistance during cyclic voltammetry experiments.

REFERENCES


