Recovery of Radioactive Iodine From Nuclear Power Plants Using a Microwave Based Plasma Technique

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Abstract—In the event of a nuclear plant accident where the nuclear fuel has been damaged, radioactive iodine gaseous species can be released into the environment. Iodine is known to migrate well thus it is possible for the iodine to enter ocean plants nearby such as seaweed and kelp. A microwave generated plasma is used to elevate the energy of the iodine molecules found in kelp to the point where ionization can occur. The characteristics of the plasma and the iodine species is observed. The released gaseous species are capture in a filter system and the iodine species are identified. The results indicate that I_2, I^-, and I_3^- species are observed. The technique works well at ionizing the iodine species at relatively low powers. These results suggest that a microwave based technique may be useful for environmental monitoring and cleanup activities of radioactive species such as iodine.

Keywords—Microwave plasma processing, iodine capture

I. Introduction

In the event of a nuclear plant accident where the nuclear fuel has been damaged, radioactive iodine gaseous species can be released into the plant environment. Iodine is a concern due to the potential for iodine to be radioactive and to attack the thyroid in humans, hence posing a health risk in the form of thyroid cancers [1]–[3].

The containment systems are designed to capture most of the iodine species and maintain the radiation within the facility. It is possible that in some severe accident scenarios, the containment systems may also fail and the iodine may be released outside the plant. Iodine is known to migrate well in both gas and liquid phases. Thus it is possible for the iodine to enter the cooling water exiting the plant and from there enter into the ocean plants nearby such as seaweed and kelp. The work of Hou *et al.* demonstrates the potential spread of an iodine release to the environment which shows that the release could impact multiple nations [4]. Knowledge of the amount of iodine present could be obtained from radiation surveys and standard chemical techniques. However, extracting the iodine in a controlled manner to recover it and remediate the environment would require a more rigourous process.

To date, iodine is captured through molecular sieves and cryogenic traps. Yet the iodine will not be present alone and the use of cryogenic traps may not be optimal due to the interference of other particles.

Some novel methods have been used to capture iodine by other methods. Stennett *et al.* considered using lead vanadium oxide compounds for immobilization of iodine radioisotopes by a microwave dielectric heating method [5]. This technique is being considered as part of a waste disposal method. Ibupoto *et al.* have developed ZnO nanotubes to function as an iodide ion sensor [6] where they claim linearity from 10^{-6} to 10^{-1} M yet this technique only detects iodine. Mahajan *et al.* [7] and Gomez Martin *et al.* [8] have used an off-resonance fluorescence technique for measurement of atmospheric iodine.

In this work, a microwave generated plasma is used to elevate the energy of the iodine molecules found in kelp to the point where ionization can occur.

Microwaves have also been used for various types of species capture. Shimamori *et al.* considered low energy electron attachment to molecules by a pulse-radiolysis microwave cavity technique combined with microwave heating [9]. Nagai *et al.* [10] at Nagoya University used 2.45 GHz microwaves to generate a plasma for the decomposition and polymerization of perfluorinated compounds. The species involved were He, CF_4, C_4F_8, H_2 and trace N_2. The size of the species is of similar interest to our work. The main value was the breakdown of the CF bonds and formation of new species.

The use of microwave energy for the generation of plasma has also been studied under various conditions. Hattori *et al.* used microwaves to pass energy through a rod and form plasmas at the rod tip in water solutions [11]. Jasinski *et al.* studied the use of microwave plasma sources for the generation of hydrogen [12]. Tatarova *et al.* studied microwave air plasmas under atmospheric pressure conditions [13]. Deng *et al.* considered direct current plasma jets at atmospheric pressure conditions [14]. Hrycak *et al.* used microwave methods for generation of plasmas in different types of gases at atmospheric pressure [15]. Mizeraczyk *et al.* used atmospheric-pressure microwave plasmas for the processing of gaseous species [16]. The above works have demonstrated that microwave plasmas can be formed at or near atmospheric conditions and can be used for the breaking of chemical bonds and the charging of species.

II. Methodology

The experiments conducted in this work consisted of preparation of the Kelp-Iodine sample, generation of a microwave

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Presented at the 10th International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy, in August 2016

$Ar \rightarrow Ar^{**} \rightarrow Ar^{+} + e^{-}$ Ar^{*}	Ionization Excitation
$Ar^{*} + KI \rightarrow KI^{**} \rightarrow KI^{+} + e^{-}$ $K + I$	Penning ionization Dissociation
$KI^{+} + e^{-} \rightarrow K + I$	Recombination
$I + I \rightarrow I_2$	Radical reaction

Fig. 1. Key reactions present in the argon based plasma.

based plasma for iodine reaction, capture of the iodine species, and analysis.

While different sources of iodine are possible for this work, kelp is chosen as a candidate material relatively available in Japan. Kelp is known to grow in large quantities near the outflow of nuclear power plants and kelp is known to naturally absorb iodine usually in the form of potassium iodide [17].

The kelp is baked in a crucible under a bunsen burner until all moisture is driven off. The result is a dried and burnt kelp that can be crushed with mortar and pestle to produce an ash. The kelp ash can then be placed into the plasma stream for processing.

Argon gas is used as the base component of the plasma as the ignition power for the plasma is lower than for some other gases and argon is relatively inexpensive. Note that while the plasma is predominantly argon, other species are present such as carbon and iodine. The plasma is used to excite the argon to a metastable state. The metastable argon interacts with potassium iodide via Penning ionization resulting in the dissociation of the potassium and iodine species. The dissociated iodine can undergo another reaction to form I_2. Fig. 1 shows the key reactions of concern for this work that are present within the plasma or shortly downstream of the plasma. Further combinations of I^{-}, and I_3^{-} can also occur.

A. 2.45 GHz microwave system

The experimental set-up used in this study consists of two parts: The Microwave System and the Plasma Test Section. The microwave system used is shown in Fig. 2 and consists of a microwave generator, isolator, monitoring unit, wave guide tuner, and test cell.

The microwave generator is a 2.45 GHz, 1.3 kW continuous wave magnetron type generator. The unit was manufactured by Kyoto Micro-Densi Co. Ltd in Japan [18]. It is capable of pulse power up to 2 kW at a power source of 200 V under 50 or 60 Hz conditions.

The system measures the forward and reflected power and allows for adjustment of the microwave through the wave guide tuner.

The test cell is the actual chamber of research interest. Inside this chamber, the microwave will reflect off the far wall. An adjustment knob further tunes the microwave to minimize reflected power and adjust the focal point in the test section. In the center of the actual chamber, is a circular penetration. The

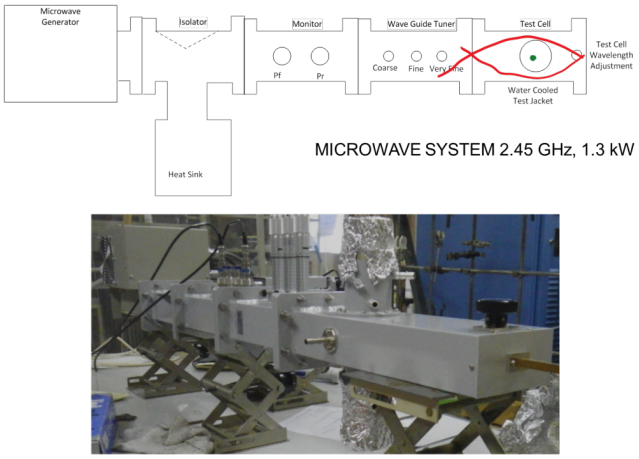

Fig. 2. Schematic and image of the 2.45 GHz microwave system for generation of a plasma environment.

circular penetration can receive test sections where a plasma can be formed. The jacket can also be water cooled to reduce localized heat generation.

B. Plasma test section

The microwave system performance was characterized under various different loads (glass tubes, different gases and different flow rates, etc.). Experiments were conducted using pyrex and quartz tubing under different configurations for testing of plasma ignition.

The final experimental plasma test section is a vertical quartz tube with an igniter (plasma seed) present for generation of electrons. The glass tube had an inner diameter of 8.44 mm and an outer diameter of 10.65 mm as measured by calipers.

The lower section of the glass tube was connected to an argon tank and a gas flow rate of 2 l/min was injected through the test section. To minimize air contamination, the argon gas flow rate was run for 5 minutes to purge the test section of air. The flow rate used resulted in an average gas velocity of 0.6 m/s and a Reynolds number of 400 which corresponds to a laminar flow regime. The experiments were performed at a room temperature of approximately 13°C.

A black comet spectrometer manufactured by StellarNet-Inc [19] was used to identify the atomic spectral emissions from the plasma. This device was able to provide reasonable atomic spectra emissions from 200 nm up to 1180 nm.

For a typical experiment, power was increased to 0.05 kW, 0.2 kW and 0.4 kW to ignite the plasma condition. Note the carbon-fibre seed is necessary for low power ignition. Without the seed, higher powers are needed and usually a reduced gas pressure is also required.

Power was then increased to 0.6, 0.8 and 0.9 kW as the processing power. At this point, the coarse tuner was adjusted to improve resonance in the microwave chamber. Reflected power was dramatically reduced and the intensity of the test chamber emission in the visible light spectrum became extreme. Power was increased to 1.0 kW and then a temporal study was performed to check the stability or relaxation of

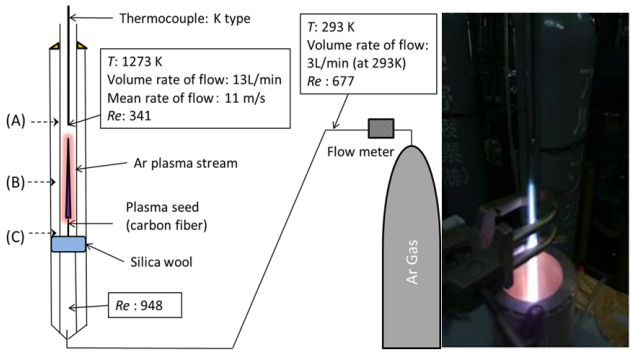

Fig. 3. Plasma test section with ignitor (plasma seed), plasma stream, and glass tubing array.

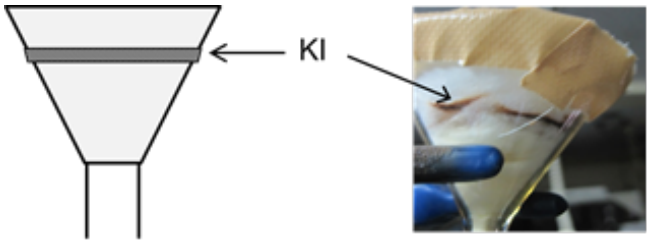

Fig. 4. Iodine trap configuration using a KI layer in a funnel to improve capture efficiency.

the microwave induced argon plasma. Experiments were then conducted at power levels of 0.8 kW to 1.0 kW.

C. Iodine trap and measurement system

Different methods were tested for trapping the iodine species. The argon gas was initially bubbled through a liquid where the water would absorb the iodine atoms. This method was found to work but was not very efficient. A typical fibre filter was built using a funnel device to trap the iodine. In some tests there was a brown discolouration occurring at the entrance of the filter section clearly capturing some of the iodine present in the system. The final trap design is shown in Fig. 4. This design consists of the basic cotton fibre filter concept. However, to increase efficiency, a layer of potassium iodide (white crystals) was placed in the filter. Stray iodine will have a higher affinity for reacting with this layer and form a then brown discolouration upon reaction as shown in Fig. 4.

The discoloured fibre (brown colour) is soaked in a solution where the iodine will be extracted and then undergoes a chemical process to remove the I_2, I^-, and I_3^- species. The resultatant solution is a pink colour and can be interpreted by colorimetry [17], [20], [21]. The solution is placed in a cuvette for analysis. Fig. 5 shows the colorimetry measurement system. A halogen lamp is used to pass light through the cuvette holder and hence the specimen. A stellarnet blue wave spectrometer is used to measure the colour spectrum. The intensity of the colour spectrum is proportional to the concentration of the various iodine species.

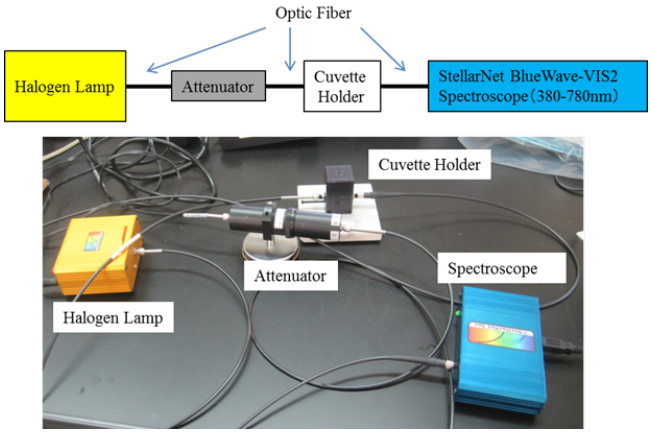

Fig. 5. Colorimetry system for measurement of iodine concentration.

III. Results

A. Plasma characteristics

Argon based plasma's were ignited from 50 W up to 0.8 kW depending upon the tuning configuration of the microwave chamber and the nature of the plasma seed in the system. Usually, plasma ignition occurred at a high power and then the microwave system was tuned to reduce the reflected power. Once the tuning was adjusted, later ignitions, even from cold conditions would occur at a lower power. If a plasma seed was present in the test chamber, in this case a small amount of free carbon fibre, then ignition was often at low powers. Note that while the ignition did occur at low powers, a previous study [22] showed that the strength of the plasma for exciting other species such as carbon, nitrogen, cesium, or iodine remained weak until 0.4 kW of applied power. At that point, the plasma conditions were sufficient for processing applications.

Fig. 6 shows the gas temperature immediately downstream of the visible argon plasma stream where the configuration is as shown in Fig. 3. The temperature is measured by a metal sheathed K-type thermocouple. The gas temperature at a low power of 0.2 kW was around 575K. The gas temperature increasing linearly with increasing power. These results are similar to the work obtained by Jasinski and Mizeraczyk [23]. In their work, they generated a plasma sheet in a quartz rectangular channel using a microwave under similar conditions to this work. The main difference is that their work used a channel where our work used a tube. For a power of 250 W, they observed gas temperatures ranging from 673K to 1073K for plasmas of similar strength and size as ours [23].

Fig. 7 shows a typical spectrum observed by the black comet spectrometer. The spectra are interpreted using the NIST database [24]. The spectrum for all power conditions is used in a Saha plot formulation to obtain the characteristics of the argon plasma. A typical Saha plot is shown in Fig. 8. The resultant argon plasma temperature varies with applied power in the range of 1800–2480K. These temperature ranges are lower than observed in other work where temperatures are observed from 2500K to 8000K [13], [14], [16] although Deng *et al.*'s work with nitrogen is close to our temperature range. In the other work, where there were multiple species were

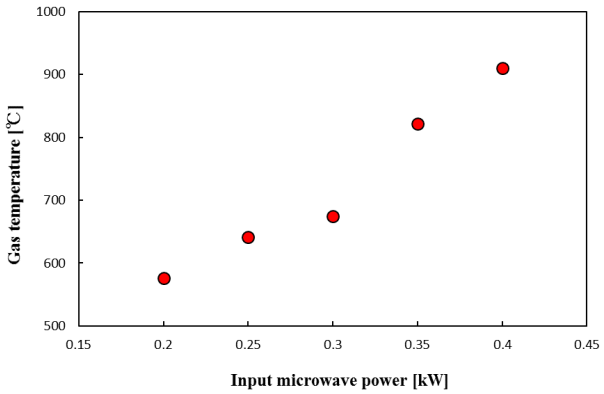

Fig. 6. Typical argon gas temperature downstream of the plasma stream.

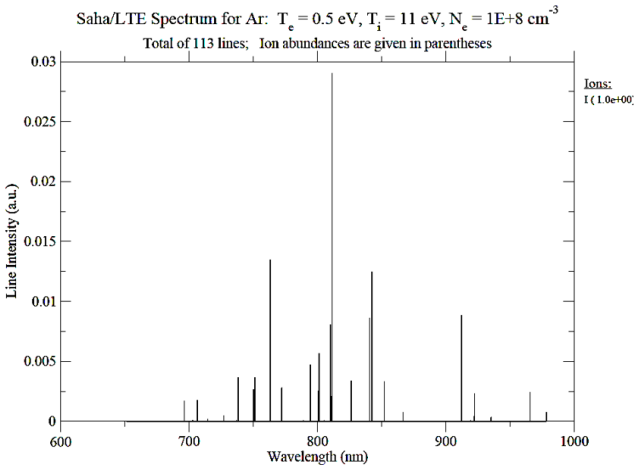

Fig. 7. Typical argon spectra for measurement of plasma conditions.

present, the plasma temperature is apparently cooler. In our case, the main argon plasma contains many other species aside from argon and the iodine of interest. It is suspected that the presence of the additional species is responsible for the cooler plasma temperature.

B. Iodine calibration

Measurement of iodine concentration is obtained by relating the concentration of iodine species in solution to the associated colour. Solutions of potassium iodide were prepared of different concentrations. KI mass from 0.33 mg to 2.62 mg was used. These solutions were chemically processed to isolate the iodine species. The resultant solutions appear pink as shown in Fig. 9 where the higher the concentration, the darker the pink colour.

The spectral response or absorbance is wavelength dependent as shown in Fig. 10. The stable iodine compound (I_2) absorbs at a peak of 515 nm. The negative ion (I^-) absorbs at 227 nm. The complex ion (I_3^-) absorbs at the two wavelengths of 288 nm and 350 nm. However, the concentration of the various species is also dependent upon the choice of solution.

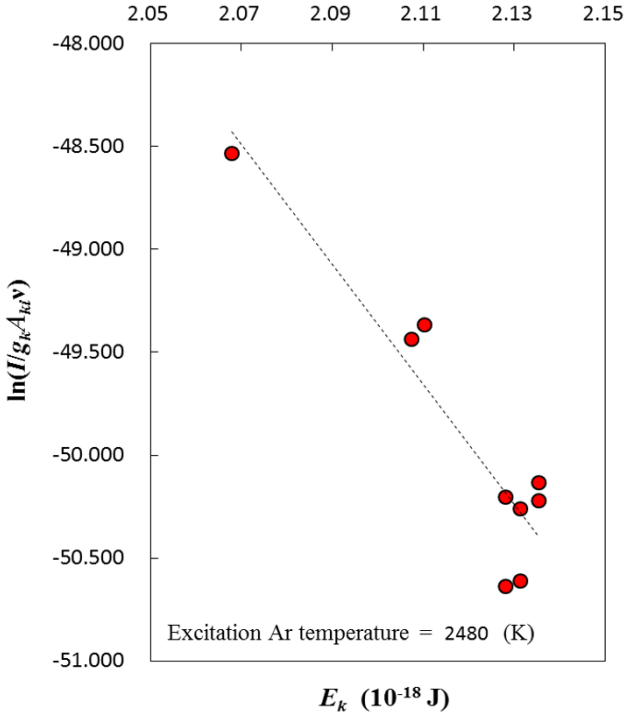

Fig. 8. Typical Saha plot for determination of plasma temperature. Applied power 0.4 kW.

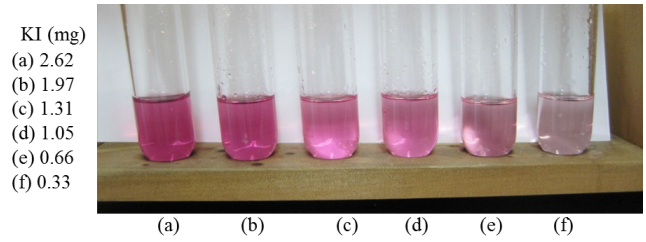

Fig. 9. Solution colour for different concentrations of KI from high to low.

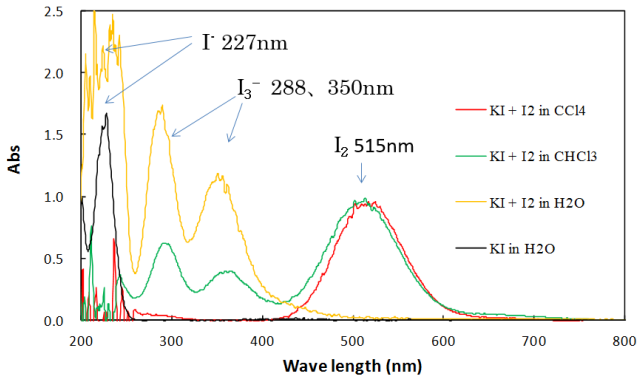

Fig. 10. Absorbance spectra for different iodine species in solution using a colorimetry technique.

KI in water will predominantly show a negative iodine ion and no other combinations. However, when excess I_2 is present, then all three species are possible. In the case where CCl_4 is used for the solution, only the I_2 compound can be

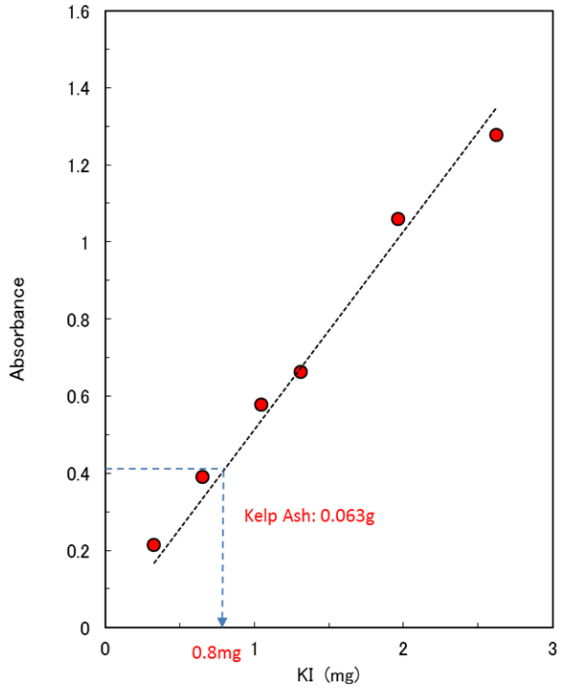

Fig. 11. Relationship of absorbance to concentration of iodine.

observed. When $CHCl_3$ is used, again all three species are present.

Each solution is processed and the peak values are obtained to establish a calibration. Fig. 11 shows the calibration results of absorbance versus mass of KI in solution. The results are essentially linear.

C. Iodine capture

Once the calibration is established, reasonable quantitative measurements can be obtained of the amount of iodine recovered from samples of kelp. The kelp ash was placed in the plasma test section shown in Fig. 3 in different configurations. In some experiments, the kelp was part of the plasma seed. In other experiments, the kelp ash was allowed to behave as part of a fluidized bed for improved interaction or was confined inside glass wool downstream of the visible argon plasma stream. In all cases, iodine was liberated from the ash suggesting that the ion species generated by the plasma are present beyond the visible spectrum.

Several experiments were performed with the cotton fibre to capture the iodine species and were successful in trapping a brown coating in the filter. Note that the quartz tubing between the plasma stream and the filter also coated with either a brown film or a white film dependent upon which of the iodine species was most prevalent. Brown was usually an I_2 compound while white contained ions.

The final kelp ash experiment used 0.063 g of kelp ash in the plasma system. The filter contained the KI layer trap to obtain a higher capture rate. Note that the KI trap layer without iodine present in the plasma would only produce a I^- peak. The kelp ash experiment demonstrated all four peaks and hence all species were present. The colorimetry system was used and the absorbance calculated to determine that 0.8 mg of equivalent KI iodine was contained with the kelp ash sample as shown in Fig. 11.

IV. Discussion

The results show that the iodine is present within the kelp ash and that the use of a microwave plasma is able to liberate the iodine. Chemistry methods can be used to isolate the iodine in solution for concentration measurement via colorimetry.

That said, the iodine is also depositing inside the system as the gas flows away from the plasma stream. Typically the outer surface temperature of the glass is dropping significantly due to air cooling in the experiment and thermophoresis effects are depositing the iodine species along the tube. The brown and white colours represent different types of iodine deposits which clearly shows that the thermophoresis phenomena affects each species differently. The result is that temperature plays an important role in the separation phenomena.

The thermophoresis effects can likely be reduced by insulating the glass tubing and moving the location of the filter closer to the plasma stream. Interim results measuring the concentration of the iodine along the test section indicate that the concentration decreases slowly along the length and that very little iodine is observed after the trap. The ash is also not completely consumed at the end of the experiment indicating that the amount of iodine measured in the trap is a small portion of the total amount of iodine available. This implies the current technique could be very useful for monitoring purposes but that further refinements are necessary if the intent is separation of radioactive species from waste material.

While the plasma conditions are well established at a modest power of 0.4 kW, further experiments may need to be performed to determine if higher applied powers would result in a stronger concentration of metastable argon. Thus different power levels may result in different efficiencies.

V. Conclusion

In this study, experimental investigations were conducted to determine if iodine could be extracted from kelp ash using a microwave plasma. The results show that:

1) Plasma ignition could be obtained at 0.05 kW;
2) Stable iodine generation was found at $\geq$0.4 kW with a small dependency upon further increases in applied power;
3) I_2, I^-, and I_3^- species can be observed as products of the plasma processing and can be separated. A linear relationship with colour can be used to quantify the amount of captured iodine.
4) Thermophoresis effects were dominant immediately downstream of the ignition point as some iodine products were deposited on the walls of the glass tubes.
5) A microwave based technique may be useful for environmental cleanup activities of radioactive species such as iodine.

ACKNOWLEDGMENT

The authors wish to thank F. Nakayasu and K. Kume for valuable discussions. This work was supported by Intramural Special Research Grant from Fukui University of Technology and a Visiting Researcher Grant from Fukui prefectural government, Japan and The Wakasawan Energy Research Centre in Tsuruga, Fukui Prefecture, Japan.

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