THE DEVELOPMENT OF METAL RECYCLING TECHNOLOGY FOR DECOMMISSIONING WASTE

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ABSTRACT

Nuclear Power Engineering Corporation (NUPEC) has been developing techniques of metal recycling for decommissioning waste, under the consignment by the Ministry of Economy, Trade and Industry (METI) of Japan. To separate activated nickel and cobalt from iron pyro-metallurgically, three methods are tested, The High-Temperature Solvent Extraction Method, The Oxygen Sparging Method and The Molten Salt Electrolysis Method. This paper describes the test results and process evaluations of these methods.

INTRODUCTION

The metal waste generated in decommissioning of a nuclear power reactor is divided roughly into a radioactive metal (activated or contaminated) and a non-radioactive metal.

For recycle of the radioactive metal waste, NUPEC is advancing technical development from 1996 based on the following scenarios.

(1) "High beta-gamma" waste is packaged in the disposal container, without adding processing
(2) Low level radioactive waste (LLW) is disposed like in trench after reducing by decontamination etc. Residual of LLW is melted and filled up the "high beta-gamma" waste package.

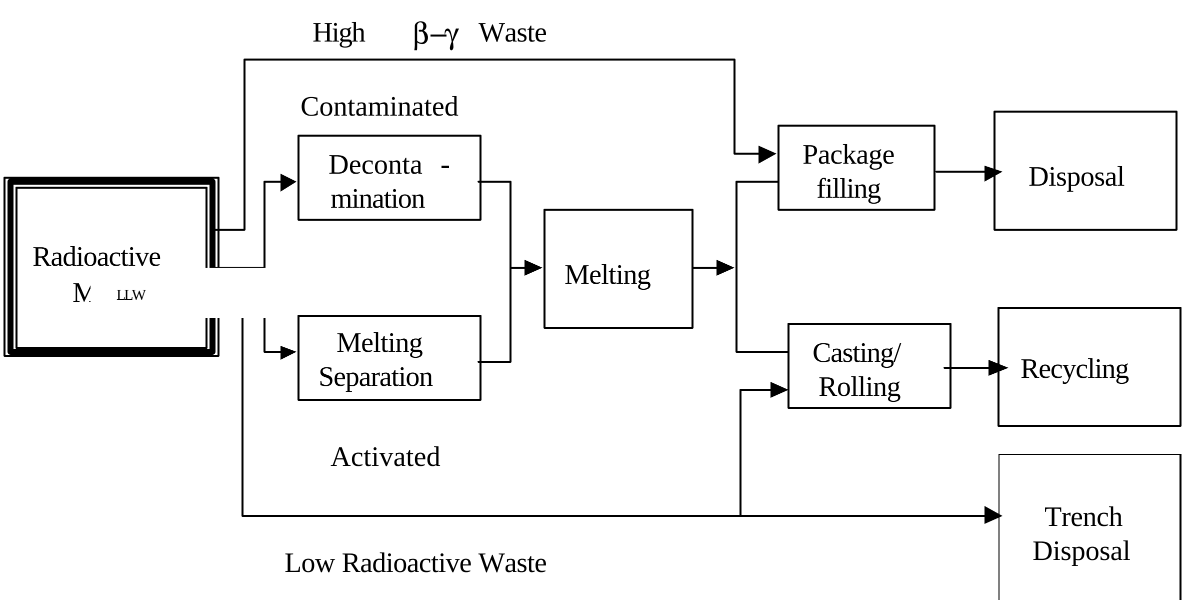

Fig.1 Recycling Scenario of Radioactive Metal

Melting separation technology is the technology of separating the element containing the radioactive isotope in the radioactive metal waste, and reducing concentration of radioactivity. This technology is carried out for the decontamination of the depth direction, the chemical and/or mechanical decontaminating method being the technology of removing the contaminant on the surface of material.

The metal waste is contaminated or radio activated by radioactive element, estimated mainly Co-60 and Ni-63. Cobalt,nickel and iron have the character like also physically and chemically because of a homology on a periodic table. Therefore, it is thought that an economical s eparation of them metallurgically is difficult until now.

In this development, our objective is establishing the technology that can be processed more economically than disposal, because the cost of disposal of radioactive waste is comparatively high.

To recycle the metal after separation processing effectively, the target performance of the methods were set up as follows.

- -DF: more than 100
  (DF is an element concentration ratio before and behind processing, and DF of cobalt is displayed like DFCo.)
- -Recovery rate: more than 60%

The present condition of development about the three methods by which practicality accepted as a result of the basic examination carried out until now is introduced to below.

HIGH-TEMPERATURE SOLVEVT EXTRACTION METHOD

Outline

High temperature solvent extraction method is the method that using the monotectic reaction and utilizes the difference of distribution ratio of solute element.

Tin-lead alloy (Sn+Pb) is used for solvent element because of forming the 2 liquid phase coexistence system with stainless steel and carbon steel

Moreover, the carbon and silicon with the difference of the affinity to separation elements and recovery metal are used for the extractor element.

This method consists of an extraction process and a reverse extraction process.

At the extraction process, carbon as an extractant is added into metal waste and the alloy (Sn+Pb) of a solvent, they are melted at about 1300 degrees C to raise distribution ratio of the separation element.

At the reverse extra ction process, the silicon as an extractant is added to the solvent after the extraction process, and the separation element is extracted.

(Sn+Pb) alloy is re-used at the extraction process.
A target performance is obtained by repeating this process (Fig. 2).

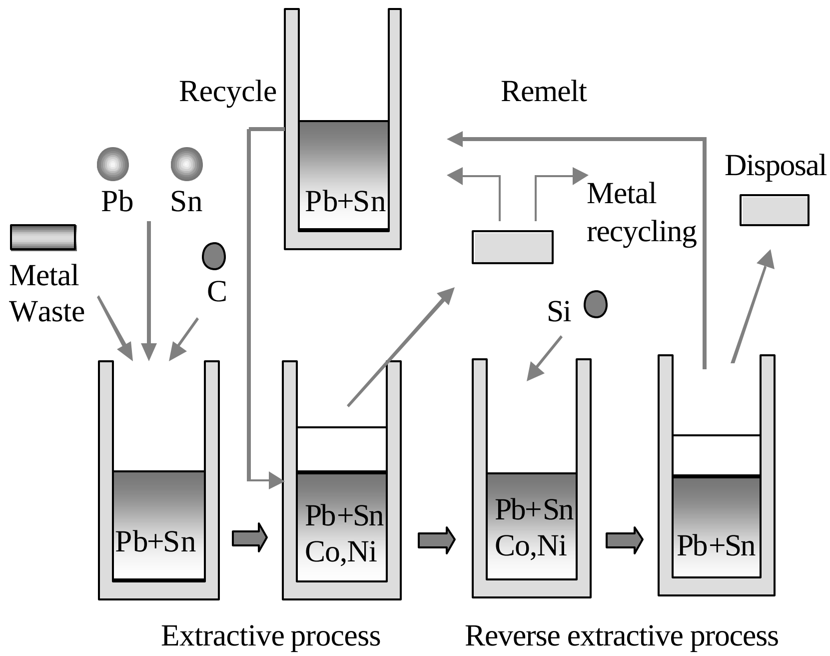

Fig.2 Diagram of Dry Extraction Process

Experimental procedure

The sample that was simulated as decommissioning metal waste, and the solvent (Sn+Pb) were melted in the 30kW, 3kHz vacuum induction-melting furnace under argon atmosphere and 1 atmospheric pressure.

Stainless steel and carbon steel with cobalt up to 1w% were used for the simulated metal waste.

In order that a melting crucible might maintain an extract phase at carbon saturation, carbon crucible was used, and the total amount of dissolution was set to 3kg.

Carbon steel was melted and kept at 1400 degrees C for 20 minutes for homogenization, and after holding at 1300 degrees C for 15 minutes, it was cooled to solidify.

Stainless steel was kept at 1450 degrees C for 15 minutes in consideration of its melting point rise by chromium mixing, and then it was held 1400 degrees C for 20 minutes.

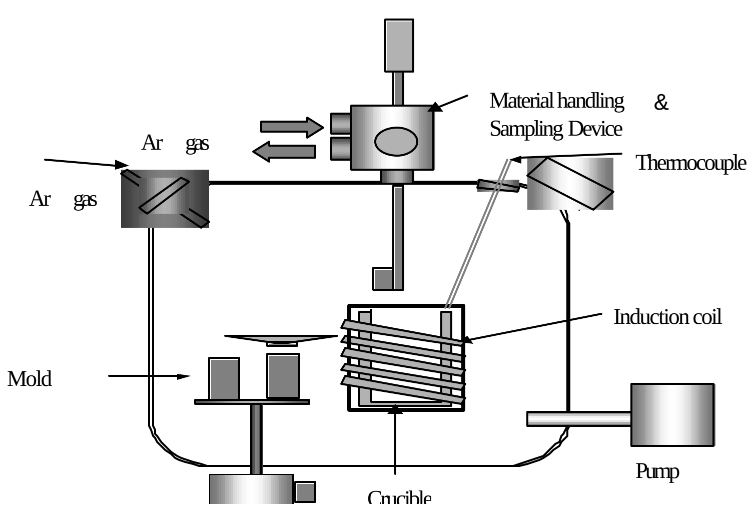

Fig.3 Schematic Drawing of Dry Extraction Experiment

Experimental results

The amount of Pb was changed to decide the optimum rate of Pb in an alloy (Sn+Pb). It was found that 48% composition of Pb was the optimum value on a recovery performance.

Next, the examination which makes the (Sn+Pb)/Fe ratio of the amount of solvents optimize was carried out, and our target performance could be obtained by (Sn+Pb)/Fe = 30.

The influence of repetition processing was examined on the above conditions. Consequently, DFCo=10 or more and Fe recovery rate=60% or more were obtained by the four number of times of repetition for carbon steel.

For stainless steel, DFNi=100 or more and Fe recovery rate=60% or more, our target value, were obtained by the two number of times of repetition. But it was presumed that the number of times of repetition processing was required 6 times to make DFCo=10 or more, and the recovery rate fell to 30% at that times.

In actual decommissioning waste, mixing of electric wiring, window frames sash, etc. is assumed. For this reason, an impurity addition examination (Cu and aluminum respectively 1%) was carried out to examine the influence of very small quantity of element in material. The solvent extracted about 50 percent of aluminum

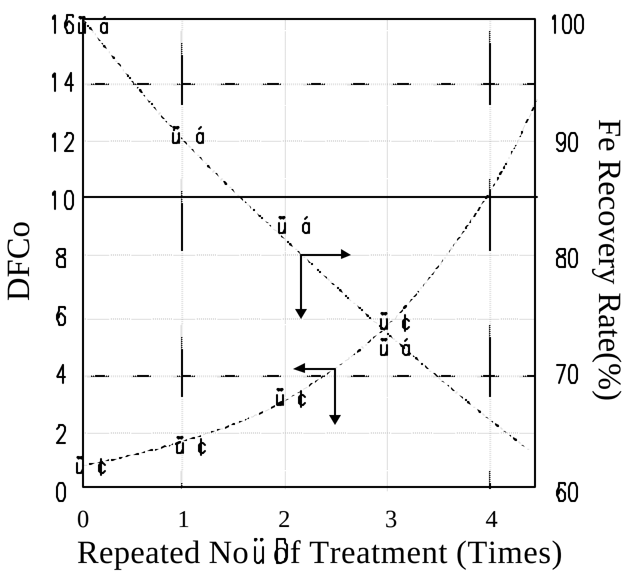

Fig.4 Relationship between DFCo, Fe Recovery Ratio and Repeated Number of Treatment (Times)

OXYGEN SPARGING METHOD

Outline

Oxygen Sparging Method is the metal recycling process that uses a pyro-metallurgical metal separation technique (without radio nuclides). This process utilizes the difference of the oxygen affinities between metals (Fig.5).

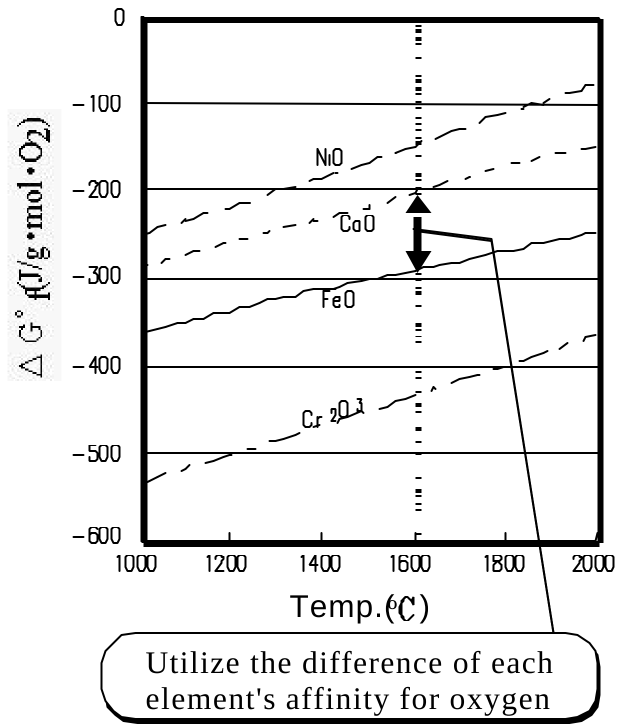

Fig.5 Principal of Oxygen Sparging Method

Fig.6 shows the concept of this method. After the waste is melted and sparged by oxygen gas, chromium and iron are oxidized prior to nickel and cobalt, and form a slag phase in the oxidation step. The slight amount of nickel and cobalt oxidized and contained in the slag are reduced in advance by controlling the reductant amount in the following first reduction step. The slag that contains chromium and iron are reduced to the recycled metal in the second reduction step. These double separation steps enable the effective separation of metals.

The temporary goal of this testing is that the decontamination factor (DF) of nickel and cobalt is more than 100 and that metal recovery ratio is more than 60%. According to a previous cost calculation, it has been found that enough profit could be gained by achieving these goals.

The second reduction slag will be a waste if it is not reused. Therefore it is important to confirm that the slag can be reused as a flux in the oxidation step to minimize the amount of the waste.

This paper describes resentstudy that concentrates on treatment of carbon steel and has target value of 100 for DF Co along with 60 for metal recovery ratio.

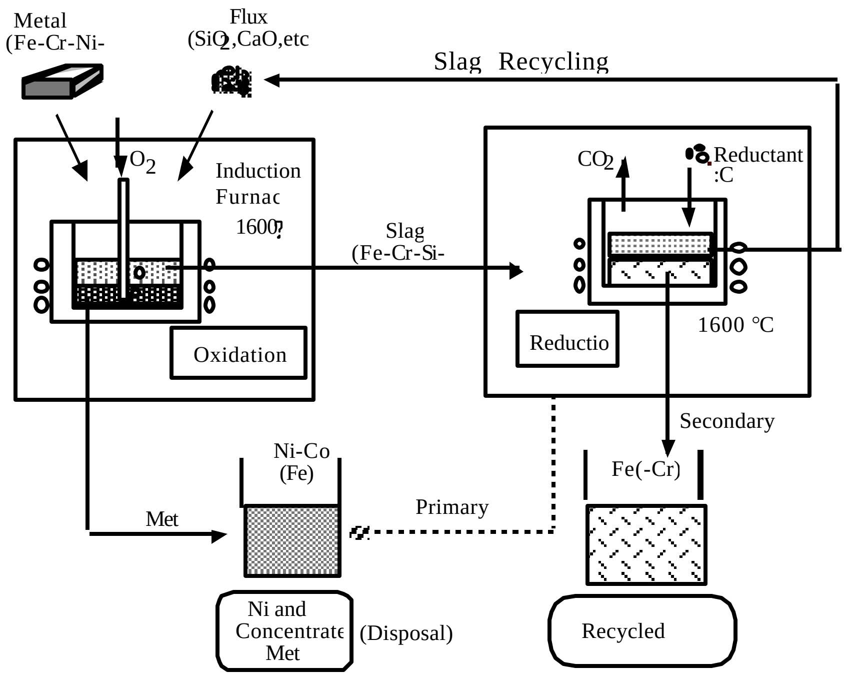

Fig.6 Concept of Oxygen SpargingMethod

Experimental procedure

The experimental apparatus used on 3 kg/scale tests is shown in Fig.7. This is an induction furnace with triple crucibles, the magnesia crucible with a volume of 2,500 cm3, the graphite crucible heated by induction and the alumina holder.

Through some preliminary experiments, it had been found that magnesia had showed a much better corrosion resistance than boron nitride, alumina and yttria coating alumina under the oxidizing conditions.

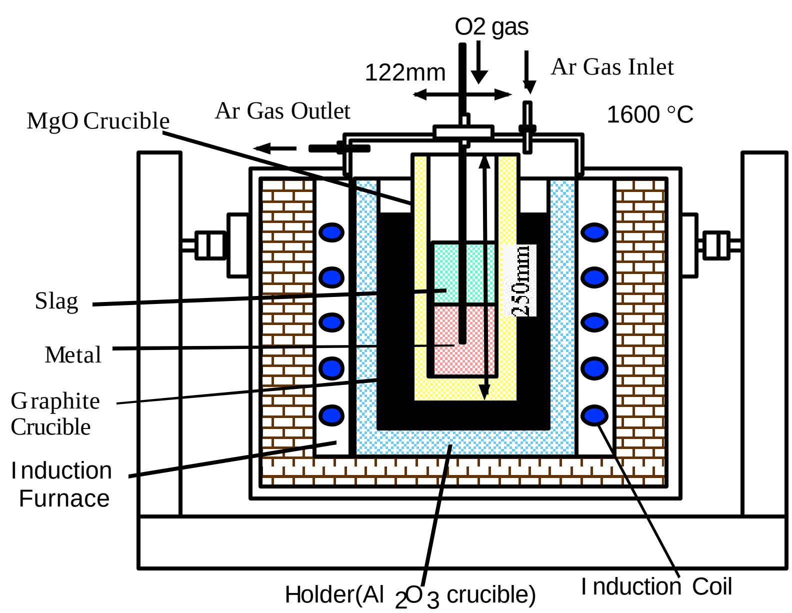

Fig.7 Schematic diagram of 3.0 kg scale apparatus

The experimental equipment for 20kg/scale test is shown in Fig.8. The equipment is composed of an induction furnace, a ladle and an exhauster.

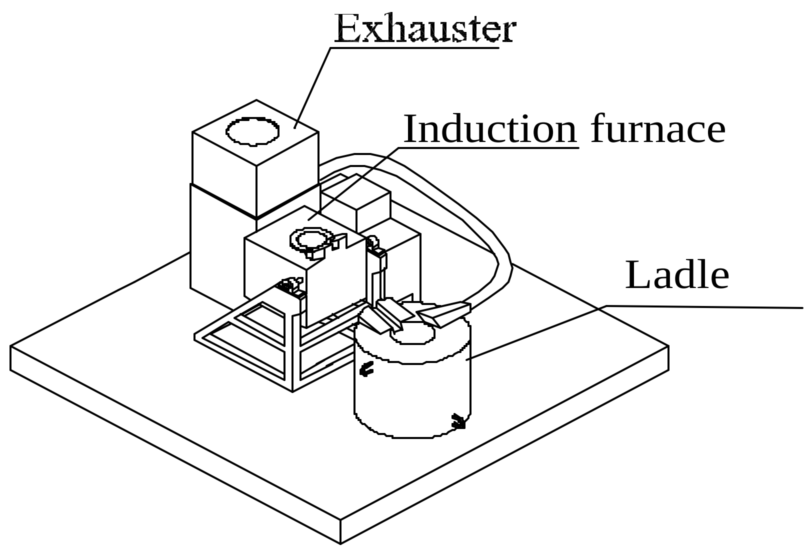

Fig.8 20kg/scale Test Equipment

Experimental results

Fig.9 shows the decontamination factor of cobalt for 3kg/scale test and scale-up test respectively. These tests were conducted with 1 wt% of cobalt content in raw materials.

As for the 3kg/scale test, DFCo was 110 and the metal recovery ratio was 72. Both values satisfied our target values. As for the 20kg/scale test, DFCo was 100 and the metal recovery ratio was 56, which almost reached our target value.

Fig.10 shows decontamination factor and recovery ratio for 3-kg/scale test under the condition that Co concentration in raw material is 0.03wt% which is actual Co concentration level in carbon steel. DFCo was 100 and recovery ration was 72, which satisfied our target value.

As for stainless steel, we conducted 3kg/scale test as one for carbon steel. Composition of slag has to be changed because of high concentration of chromium compared with one in carbon steel.

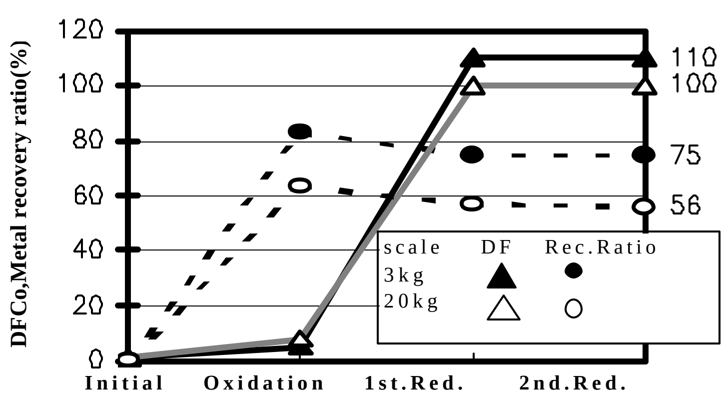

Fig.9 DF and Metal Recovery Ratio
(Initial Co Content 1%)

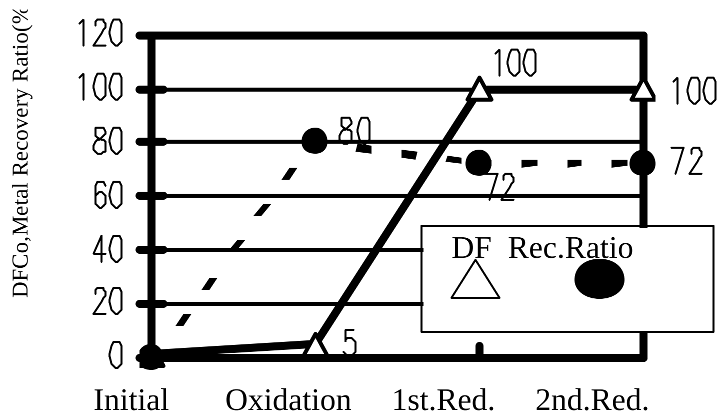

Fig10. DF and Metal Recovery Ratio
(Initial Co Content 0.03%)

MOLTEN SALT ELECTROLYSIS METHOD

Outline

Molten salt electrolysis method uses activated metal waste as an anode. Cobalt and nickel contained main radioactive element are electrolyzed in a molten salt which is a solvent. Slime is collected with a diaphragm and dissolved elements are extracted in lead. Recovery iron and chromium are collected as a deposit of a cathode.

As a process, recovery metal is extracted preferentially in about 500 degrees C molten salt (LiCl-KCl), using the difference of the oxidation-reduction potential of separation elements and a recovery metal.

Cobalt and nickel which are not dissolved are held in a diaphragm as slime, and both cobalt and nickel ion are extracted in lead as a metal by the substitution reaction with lead using the difference of the generation energy of a chloride (Fig. 11).

Combined use is also possible although examination of a diaphragm process and the lead extraction was carried out separately.

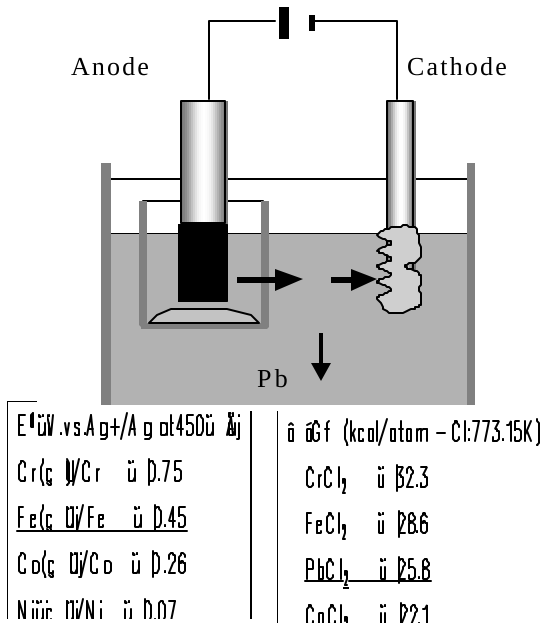

Fig.11 Diagram of the Molten Salt Electrolysis Method

Experimental procedure

In the diaphragm process, 1100g of LiCl-KCl-FeCl3 were loaded into to a vertical electrolysis cell of Pyrex.

Stainless steel added cobalt (not radioactive element) at 1%, which simulated decommissioning metal waste and has a shape of 100mmL, 20mmW, and 3-4mmt was used as an anode. A bar of stainless steel with a diameter of 5mm was used as cathode.

The diaphragm for collecting slimes is a quartz filter. The reaction crucible loaded the chloride was heated at 500 degrees C in argon atmosphere. In this condition, the electrolysis with constant current was carried out. In the lead extraction examination, iron, chromium, nickel, and cobalt were put into molten salt as the chloride, and the process in which cobalt and nickel were extracted in lead was measured as an aging of concentration of each component.

Experimental results

By diaphragm electrolysis examination, DFCo=100 or more and DFNi=700 or more were obtained (Fig. 12).

DF fell without diaphragm because the slime containing the separation metal generated by the anode floated and moved in the inside of an electrolysis salt, and adhered into the cathode-deposition material. This shows a quartz filter diaphragm is effective to prevent the slime moving to the cathode.

By the lead extraction examination, DFCo=10, DFNi=50 or more for stainless steel and DFCo=50 or more for carbon steel were obtained (Fig.13).

From the above result, supposing the process which combined a diaphragm and lead extraction, the combination performance was calculated By multiplied both above DF, DFCo=500 or more, DFNi=20,000 or more for stainless steel and DFCo=500 or more for carbon steel were supposed Moreover, the recovery rate was presumed 80% or more.

By the electrolytic-winning examination which deposits a recovery metal by electrolysis from the molten salt in which the object metal was melted as a chloride, DFCo=10,DFNi=2 for stainless steel, DFCo=10 for carbon steel were obtained. (Fig.14)

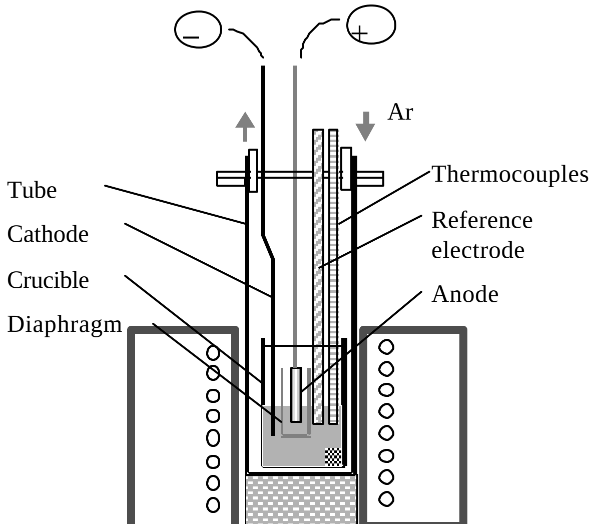

Fig.12 Schematic Drawing of Diagram Electrolysis Experiment

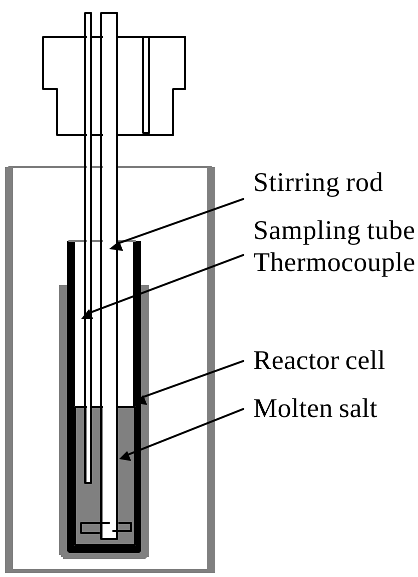

Fig.13 Schematic Drawing of Lead Extraction Experiment

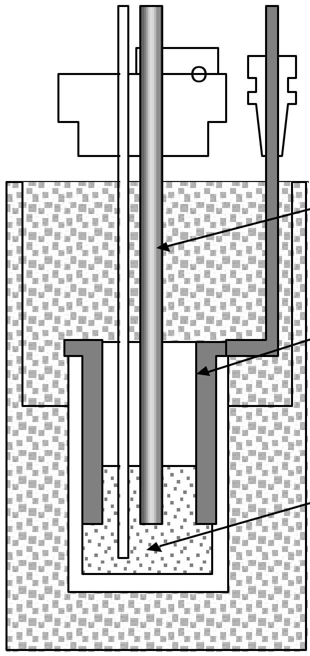

Fig.14 Schematic Drawing of Metal Recovery Experiment by Electrolysis

CONCLUSIONS

The following things became clear as a result of the basic examination about metal recycle technologies.

(1) The high temperature solvent extraction method

DFCo=10 or more and Fe recovery rate=60% or more were obtained by the four number of times of repetition processing for carbon stee l.

For stainless steel, the recovery rate fell to 30%.

(2) The oxygen sparging method

With carbon steel containing cobalt of 1wt%, DF Co for 3kg/scale test and 20kg/scale test were more than 100, which satisfied our target value. The metal recovery ratio for 3kg/scale test was more than 60, and one for 20kg/scale test was 56, which almost reached our target value.

With carbon steel containing cobalt of 0.03 wt% for 3kg/scale test, DF Co of more than 100 and the metal recovery ratio of more than 60 were achieved. These values satisfied our target value.

(3) The molten salt electrolysis method.

It can be expect that DFCo becomes 100 or more by combined use of the diaphragm and lead extraction.

ACKNOWLEGMENTS

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