THE EXTRACTION OF HEAVY METALS BY MEANS OF
A NEW ELECTROLYTIC METHOD(*)

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ABSTRACT
The extraction of metals in known metallurgical methods is pursued on the basis of separating as much as possible the desired metal’s content from the ore concentrate, in the most economical manner. When these principles are also applied to the extraction of heavy metals, the related environmental factors do not readily meet with requirements. Today, an acceptable extraction technology for metals must satisfy the need to produce the deep separation of metals from their source in both economical and environmentally safe manner. This pertains to the direction of our ongoing research and development, among others in the field of environmental remediation. Earlier, we successfully addressed in an environmentally safe manner the selective extraction of radioactive isotopes from liquid radioactive wastes, produced at Armenia’s Metzamor Nuclear Power Plant and implemented a functioning LRW station at the NPP. Currently, we extended our new electrodialysis-based electrolytic method in a laboratory scale, for the extraction and deep separation of different metals, including the heavy metals. Our new method, its efficiency, economy and full compliance with environmental issues will be presented.

INTRODUCTION
A newly developed hydro-chemical metal extraction and purification system, presented in this paper, is a result of proprietary work performed at AREV Scientific-Industrial Company in Yerevan, Armenia. This technology was initially developed especially to secure the large volume of Liquid Radioactive Wastes (LRW), typically produced at Armenia’s 840-MWe Metzamor Nuclear Power Plant (NPP) or at any one of the more than four-hundred NPP operations worldwide. The extraction of metals from ore concentrates, from industrial waste waters, mineral-rich spring waters, NPP-produced liquid radioactive wastes, and in grounds contaminated by industrial wastes, in a complete, economical and environmentally safe manner, so far has not been possible, when employing the known conventional methods.

In particular, overcoming these deficiencies in a new technology would permit the efficient and economical extraction of metals from ore concentrates and the processing of globally accumulated huge quantities of liquid radioactive wastes, to take place entirely in an environmentally clean manner. AREV’s new technology development can be applied to the extraction and purification of any metal from any one of the above sources. However, we specialized to demonstrate the production of 99.99% pure molybdenum, copper, zinc and lead metals from Armenia’s ore concentrates and to the industrial-scale processing of LRW.

Key features of the new hydrometallurgical metal-extraction and refining technology are:

♦ Environmental safety—where closed-loop fluid cycles are used with hardly any emission of wastes in all the processing stages
♦ Efficient operation—with full recovery of the purified metals at low energy consumption
♦ Economical processes—with full recovery and recycling of the processing materials
NEW, ENVIRONMENTALLY SAFE PROCESSING OF LRW AT NUCLEAR POWER PLANTS

In the operation of nuclear power plants, large volumes of LRW are produced, having low to medium level of radioactivity that must be processed efficiently, to reduce their volume significantly, to permit the safe and cost-effective storage of the residual material. The current method of processing LRW is based on dehydration-evaporation that leaves behind large volumes of solid radioactive waste. The radiotoxicity of this waste is sufficiently long-lived that a safe storage of a few hundred years is still required. This situation can be removed if in the waste-product stream the long-lived radioactive isotopes are removed selectively and completely. Research to accomplish this is being pursued in several countries. Results are insufficient to solve the problem fundamentally, by removing 100% of the long-lived radioactive components.

We summarize the four existing industrial methods that so far are used to reduce the LRW volume, stating their deficiencies. Next, we present AREV’s developed new process, which is a novel Electrodialysis Separator, together with the operating experience of an industrial-scale plant that reveals the major advantages. The four currently used industrial methods have the following features:

1. The Dehydration-Evaporation Method—where the basic disadvantage is that all the radio-nuclides in the LRW are retained in the condensate and the problem of safely storing the radioactive materials persists [1].

2. The Ion-Exchange Method—where the basic disadvantages are that: a) the method can be applied only to process LRW containing salts of less than 1 g/l; b) the resins used in the ion-exchange process now become a new source of radioactive waste; and c) the amount of separation of the radioactive materials is incomplete [2-8].

3. A Partial Electrodialysis Method—where the basic disadvantages are that: a) the ions of chemical elements remain in the liquid waste, so that reduction of the radioactive liquid volume is less than in the first method; and b), practically, the amount of separation of radioactive materials does not quite meet the requirements [9-15].

4. A Complete Electrodialysis Method—where the ions of chemical elements are also extracted by the use of a mercury cathode, producing an amalgam of mercury, which results to the complete separation of radioactive materials from the LRW volume. However, the disadvantages are that: a) the mercury amalgam itself now requires further processing; and b) the throughput of the LRW cleaning process is limited by the rate of mercury amalgam formation [16-17].

A unique Electrodialysis Separator was developed at AREV, initially to overcome the above deficiencies for the processing of LRW products. This was on the basis of a three-chamber electrodialysis (ED) assembly [18]. As shown in Figure 1, the positively charged ions, the cations from the LRW electrolyte solution fed into the central processing chamber, under the influence of an applied DC electric field, are made to migrate and collect in the cathode chamber, by means of a proprietary technique that inhibits their reverse diffusion, while the negatively charged anions are made to collect at the aqueous anode chamber.

The limiting amount of separation of the ions from the working fluid to be cleaned is set by the diffusion of some of the separated ions from the cathode and anode chambers, back into the central processing chamber. The efficiency of the Electrodialysis Separator is thus increased by an arrangement that prohibits the back diffusion of the cations. The reverse diffusion of cations is entirely eliminated, which is the main reason why the extraction of isotopes becomes possible at a very high level and efficiency. The implementation of this feature is due to our innovation.
Fig. 1 – Three-Chamber Electrodialysis Separator

1 – Cathode Chamber  
2 – Electrolyte Processing Chamber  
3 – Anode Chamber  
4, 5 – Electrodes  
6 – Cation Exchange Membrane (*)  
7 – Electrodialysis Device Vessel  
8 – Anion Exchange Membrane (*)

(*) Typical membrane passage pores are 3 – 8 Angstrom (i.e. 0.3 – 0.8 nanometer), the size of metal ions. The surface density of pores is 10 million to 100 million per cm². Membranes are made of stable dielectric material.

The effectiveness of the new method can now be compared with the Dehydration-Evaporation Method and a conventional Electrodialysis Method based on the formation of amalgam of mercury, for the cleanup of liquid radioactive waste at nuclear power plants:

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Dehydration-Evaporation Method</th>
<th>Electrodialysis Method with Hg Cathode and Amalgam</th>
<th>New Electrodialysis Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric Power Use</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>LRW Volume Reduced</td>
<td>160:1</td>
<td>~ 2:1</td>
<td>&gt; 2,000:1</td>
</tr>
<tr>
<td>Processing Time</td>
<td>Long</td>
<td>Short</td>
<td>Short</td>
</tr>
</tbody>
</table>

In the following two examples of the new ED method’s applications, the extraction and refining of metals is presented on the basis of using cesium, since this is chemically one of the most active elements in nature, such that a successful demonstration with the difficult-to-handle cesium would imply an equal success to extract and refine the chemically less active metals.

The following is a summary of the separation of metals from LRW employing the ED Separator. The radioactive liquid has a density of 1.003 g/cm³ and a chemical composition that includes cleaning agents and inorganic components. The following radioactive isotopes were produced in the LRW from the operation of the Metzamor NPP:
Table II.

<table>
<thead>
<tr>
<th>Radioactive Nuclide Type</th>
<th>Specific Activity in Bequerel/liter [Bq/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs-137</td>
<td>15,000</td>
</tr>
<tr>
<td>Cs-134</td>
<td>5,000</td>
</tr>
<tr>
<td>Co-60</td>
<td>1,200</td>
</tr>
<tr>
<td>Mn-54</td>
<td>600</td>
</tr>
<tr>
<td>Na-24</td>
<td>200</td>
</tr>
<tr>
<td>Handled salt content</td>
<td>≤ 3 (g/l)</td>
</tr>
</tbody>
</table>

The LRW electrolyte (1) is introduced into the water tank (2) shown in Fig. 2, from which it is pumped into the central processing chamber of the ED Separator (4) at a rate of 50 l/hr. The electrodes consist of stainless steel plates. The ED assembly of Figure 2 had the following characteristics:

- Voltage between Electrodes: 10 Volt (V)
- Type of Membranes Used: MK-40 and MA-40 for cathode and anode sides
- Membrane Surface Area: 500 cm²
- Number of Membranes Used: 3 of each type, a total of 6
- Separation of Membranes: 0.3 cm (width of LRW processing chamber)
- Volume of Base-Solution Tank (8): 5.0 liter
- Current Density in Electrolysis Concentrator (10): 15 mA/cm²
- Volume of EC Electrode Chambers (11), Each: 30 cm³

The liquid in the Base-Solution Tank (8) is processed via the closed loop (9), in an especial Electrolysis Concentrator (10), in which the extracted metal isotopes are concentrated selectively by an electrolysis process and outputted in a solid state, in the form of a fine powder.

In the demonstration, after the unit was brought to stable operation, the separation and removal of cesium isotopes, leaving behind in the cleaned water a residual activity of < 0.3 Bq/liter, corresponded to the cesium’s residual concentration to be 10⁻¹¹ g/l. This showed a capability of ultra fine separation and collection of metals in the new method. The resultant processed liquid in the tank had a density 1.003 g/cm³ and the residual specific activity of less than 0.3 Bq/liter was consistent with the activity of the natural background at Yerevan’s altitude.
Completing this highly successful development, AREV Company designed, constructed and assembled a substantial industrial-scale plant for the processing of LRW. AREV installed and operated the facility shown in Figure 3 at Armenia’s 840-MWe Metzamor Nuclear Power Plant [19-22]. This station is now running routinely and has the following characteristics:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Footprint Area</td>
<td>100 m²</td>
</tr>
<tr>
<td>Total Weight of Assemblies</td>
<td>10 tonne</td>
</tr>
<tr>
<td>LRW Processing Throughput</td>
<td>1 tonne/hour</td>
</tr>
<tr>
<td>Electric Power Consumption</td>
<td>20 kW</td>
</tr>
<tr>
<td>Extraction of Cesium Isotopes</td>
<td>&gt; 99.9%</td>
</tr>
<tr>
<td>Cleaned Water’s Residual Activity</td>
<td>&lt; 0.3 Bq/liter</td>
</tr>
</tbody>
</table>

The entire installation is housed in three halls, consisting of the equipment hall, the high-radioactivity handling hall and a room for the automated operation where control panels and computers are located. The equipment hall contains the LRW processing front-end mechanical filter, the filters for the removal of oils from the radioactive fluid, another stage of ultra filtration, and the Electrodialysis Separator stage followed by the Electrolysis Concentrator stage, plus the storage tanks and associated other devices. The hall for the management of high level of radioactivity contains another Electrolysis Concentrator followed by the final EC ultra concentration equipment. Figure 3 is a photograph of the industrial-scale installation.
NEW, ENVIRONMENTALLY SAFE EXTRACTION AND REFINING OF METALS FROM MINERAL ORE CONCENTRATES

To demonstrate the superiority of our new method, to extract and refine metals from mineral ore concentrates [23], we again chose to employ a cesium-based electrolytic solution in the amount consistent with those concentrations expected in a hydrometallurgical process. Accordingly, we used 20 g of CsNO₃ dissolved in 100 ml of water to proceed with a laboratory-scale demonstration. Following Figure 2, the input electrolyte solution (1) was pumped into the water tank (2) at a rate of 10 ml/min, and introduced into the central processing chamber of the Electrodialysis Separator. As a result of the ED process, anions are accumulated in the acid-solution tank (3), while the cations are adding into the base-solution tank (8). The base solution was processed further in an especial Electrolysis Concentrator (10), to accumulate and refine the selected metal. The amount of metal extraction is linearly proportional to the current flowing in the Electrodialysis Separator. Following 15 minutes of operation from when the electrolyte was introduced, the electric current in the ED unit (4) dropped to a residual value of 0.007 A, from a starting current of 5 A. The amount of extracted metal was also monitored by the amount of current flowing in the especial Electrolysis Concentrator (10). Following the extraction of the cesium metal product in solid powder form, the input electrolyte was reconstituted by dissolving in nitric acid, from which 19.77 g of CsNO₃ was reestablished, as compared to the original 20 g. This difference was well within the measurement error.

The above two different demonstrations of the new electrodialysis technology show that important environmental problems, such as the removal of harmful liquid-radioactive wastes, are solved in the most economical and energy efficient manner, while a new avenue has also opened for its large-scale use in hydrometallurgy. In particular, this method has been employed at AREV to extract and refine molybdenum, copper, zinc and lead from Armenia’s mineral ore concentrates.

AREV’s corresponding hydrometallurgical plant design for the large-scale extraction and refining of base and noble metals has a very high level of environmental safety, for an industry that so far has caused considerable environmental harm. The new plant design has no smokestacks, nor the emission of heavy-metal loaded liquid residues, and its operation is characterized by high energy efficiency, which translates to high economy, while all materials used in the processing stages are fully reconstituted and recycled.

(*) This work is supported by AREV Scientific-Industrial Institute’s internal Research and Development funds. Electronic address: Zavenin@cs.com
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