INDUSTRIAL-SCALE DECONTAMINATION USING THE DECOHA PROCESS AT CHERNOBYL

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ABSTRACT

A decontamination facility with a throughput of 5,000 kg of stainless steel per day using the patented DECOHA technology is to be installed within the 30 km zone of Chernobyl. The chemical, physical, and operational characteristics of the facility are described.

INTRODUCTION

The Recytec Group of companies has, through a joint venture with the Chernobyl PO-Kombinat of the USSR, delivered a plant for the decontamination of 5,000 kg per day of high-grade steel using Recytec's patented DECOHA process. The steel input is comprised primarily of steel pipes and tubing. Although the plant was delivered for initial use at the Chernobyl site, significant needs for this same type of decontamination capability at other sites throughout the Soviet Union required that the plant be designed with an emphasis on flexibility and mobility.

THE DECOHA PROCESS (1)

The patented DECOHA Process marries important chemical processes -- metal dissolution in and electrochemical recovery of dissolved metals from a chemical decontamination medium -- into a single "closed loop" process.

Metal Dissolution

The "heart" of the DECOHA Process is fluoroboric acid (HBF_4) -- a commercially available acid produced from the washing of gases during aluminum production that is widely used for galvanotechnical applications due to its desirable properties as an electrolyte. In general, HBF_4 reacts with a metal to produce the corresponding metal-fluoroborate and hydrogen gas:

$$nHBF_4 + Me \rightarrow Me(BF_4)_n + \frac{n}{2} H_2 \uparrow \qquad \text{(Eq. 1)}$$

Perhaps equally if not more important, the HBF_4 reacts similarly with metal oxides -- generating water rather than hydrogen gas as a reaction end-product:

$$nHBF_4 + \text{Metal Oxide} \rightarrow Me(BF_4)_n + H_2O \qquad \text{(Eq. 2)}$$

The effectiveness of these reactions depends in large part upon the respective solubilities of the various metals in HBF_4. Experience has confirmed HBF_4 as an extremely powerful solvent for metals -- iron (Fe) and other important metals exhibit solubilities close to or greater than 200 grams per liter in 50% HBF_4. As each metal approaches its saturation point in HBF_4, the pH of the solution is maintained above 4 - 5 due to the formation of the salt of the acid rather than formation of the free acid.

Both the overall effectiveness and efficiency of the DECOHA Process are direct consequences of the reaction chemistry and solubility characteristics of metals in HBF_4. Using this process, thin layers of the contaminated metal can be removed from the surface of the contaminated object. Consequently, the level of damage to an object and the corresponding amount of waste produced can be minimized through process control -- removing only the depth of metal required to achieve the specific objectives of the decontamination. This process control and the kinetics of the DECOHA Process depend upon basic parameters and conditions of the application including reaction temperature, acid concentration, treatment time, metal type, activity profile (extent/depth of the contamination), condition of the surface (extent of mechanical damage), and the degree to which the HBF_4 is saturated with metal.

In order to achieve effective decontamination of metal surfaces in a reasonable amount of time, the DECOHA Process is generally applied at temperatures between 30°-98°C. Some metals, such as carbon steel, zircalloy, and aluminum, may be treated at room temperature. However, the stainless steels and nickel-alloys require elevated temperatures to produce realistic application times. Basically, the speed of the DECOHA Process follows a typical dependency on temperature -- for every 10°C increase in temperature, the reaction requires half as much time to take place. Typical removal rates range from 3 - 4 micrometers per hour at 80°C for nickel alloys in 50% HBF_4 to 20-25 micrometers per hour at 21°C for aluminum in a 5% HBF_4 solution.

Acid Regeneration

When secondary waste volumes are a major consideration of the overall decontamination objectives, electrochemical regeneration represents an effective and economically attractive option. As stated previously, with the DECOHA Process, it is possible to uniformly remove only the thickness

of the contaminated material absolutely necessary (i.e., the minimum thickness) for decontamination. This decontamination step separates the radioactivity and its associated mass *(metal)* from the remainder of the original metal objects. Therefore, when the "loaded" HBF_4 solution leaves the decontamination cell, it is primarily composed of the HBF_4 solution, the metal removed from the surface of the object(s), and the activity associated with that metal.

The basis for the regeneration itself can be represented by chemical reactions for the metal and HBF_4 in the regeneration cell. At the cathode (using iron as an example):

$$Fe^{+2} + 2e^{-} \rightarrow Fe^{0} \qquad \text{(Eq. 3)}$$

Correspondingly, at the anode:

$$BF_4^{-} + H^{+} \rightarrow HBF_4 \qquad \text{(Eq. 4)}$$

As illustrated by the chemical reactions, the radioactive metal is plated out at the cathode while the HBF_4 is simultaneously regenerated at the anode. Co-60 is also eliminated at the cathode due to chemical similarity. The regeneration can be carried out with useful electric efficiencies (10 - 30%) at pH-values of 1.8 - 2.5 and higher using 25% HBF_4. Further, the reaction can be carried out with useful electric efficiencies (10 - 30%) at pH-values of 1.0 - 1.5 using 5% HBF_4. The cathodically eliminated metals contain activity (e.g., Co-60) and are solidifiable with cement in a 50/50 mixture.

Although some of the nuclides are adsorbed on the cathode, a significant number of nuclides are not eliminated from the medium by electrochemical regeneration. Consequently, the DECOHA Process includes additional steps in which these "non-eliminatable" nuclides (e.g., Pu-, Cs-, Ce-, Ru-, Sr-isotopes) are adsorbed on the surface of suitable chemical products, precipitated from solution, mechanically removed from the decontamination process, and solidified in cement. The effect of the precipitation process on the decontamination is dependent on the nuclide composition and the precipitation reactions. Therefore, this process must be optimized on a case-by-case basis to match the objectives of the decontamination. In general, however, the final waste-volume of the decontamination is increased by only 1 - 2% due to the use of precipitation/adsorption following the electrochemical step.

DECOHA's Closed Loop Approach (2)

Figure 1 provides a simplified example of the DECOHA "closed loop" concept wherein the acid regeneration step works in conjunction with the decontamination step. In this example derived from Recytec's experiences at Chernobyl, approximately 5,000 kg of radioactively-contaminated metal are immersed in 10 m^3 of a 25% HBF_4 solution at 90° C and a pH of 2.4 - 2.5. The chemical reaction between the acid and the metal surface is allowed to proceed until the decontamination objective is met. Once the decontamination is complete, the same volume of HBF_4 solution is then used to treat subsequent batches of contaminated metal until the metal dissolved in the acid reaches an effective steady-state concentration. This concentration of dissolved metal is such that a decontamination pH between 2.4 - 2.5 is maintained. Attaining this pH is important since this provides the opportunity

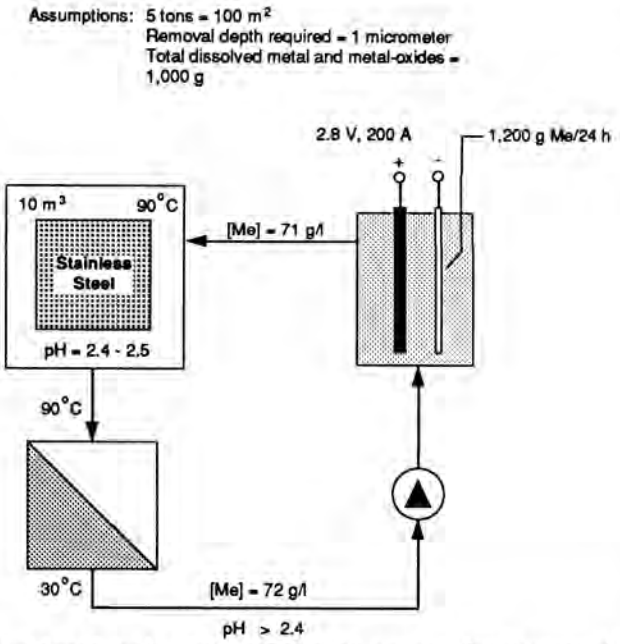

Fig. 1. Closed cycle of the DECOHA process for decontamination and regeneration in a 5 ton/day system.

for overall process optimization -- allowing simultaneously both the decontamination and regeneration processes to be effective. In the example provided, the metal concentration corresponding to this optimum condition is 72 grams per liter. This concentration of dissolved metal is still significantly below the saturation capacity of the HBF_4.

Once this steady-state condition is achieved, the DECOHA Process is converted from a batchwise decontamination process using the same acid repeatedly to a continuous flow process in which the acid is continuously recycled as batches of metal enter and leave the system. The metal-bearing acid is slowly drained from the reaction tank and allowed to cool to 30° C. The pH of this solution rises above 2.4 as a result of the temperature change. The cooled metal-bearing acid is pumped continuously to the regeneration cell where the radioactive metal is plated out at the cathode -- in the example at a rate of roughly 1,200 grams per day (1,000 grams + 20% reserve margin). The resulting metal-bearing HBF_4, now with a lower metal concentration of 71 grams per liter and a pH of 2.4, is transferred back into the decontamination cell.

Although somewhat simplified, this example provides a good indication of the mechanism by which the DECOHA Process works. The metal is decontaminated strictly on a batchwise basis. However, once a suitable concentration of metal and pH are achieved, the HBF_4 is regenerated on a continuous basis.

In order to optimize the overall "closed loop" process, the DECOHA Process takes into consideration the characteristics of the two individual process-steps:

- Rapid decontamination is achieved at low pH where a high concentration of HBF_4 and a high temperature are employed. However, the effectiveness of the electrochemical regeneration (measured by current efficiency, CE) is poor at low pH.
- Operating at high pH provides an excellent current efficiency in the electrochemical regeneration step.

Despite these apparently contradictory process requirements, a wide range of possible process conditions do exist which allow effective decontamination and regeneration to take place simultaneously. The most effective process parameters from this set of possible conditions depends upon the objectives of the decontamination and, therefore, must be optimized for each specific application. Figure 2 provides an example application (stainless steel using a 25% HBF_4 solution) and illustrates how the overall process is optimized:

- At pH = 1, the metal concentration approaches 40 g/liter and the rate of surface removal exceeds 0.8 mg/cm^2-h. However, the current efficiency of the regeneration step is below 5%.
- At pH = 3.5, the current efficiency of the regeneration step exceeds 80%. However, despite this high current efficiency and the fact that the metal concentration exceeds 80 g/liter, the rate of surface removal drops well below 0.05 mg/cm^2-h.
- Figure 2 does, however, illustrate a realistic range of workable solutions. At pH levels between 2.0 - 2.5, the current efficiency can be maintained between 15 - 35%; the metal concentration between 65 and 75 g/liter; and the surface removal rate between 0.15 - 0.35 mg/cm^2-h.

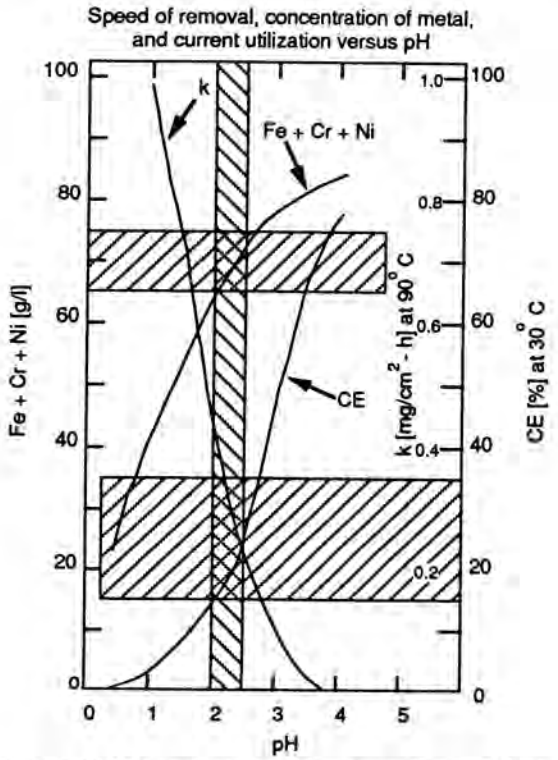

Fig. 2. DECOHA process working range for stainless steel in 25% HBF_4.

Figure 2 reflects the underlying philosophy of the DECOHA approach for decontamination of metal surfaces: to provide a method that, independent of application, can achieve free release limits for metal while at the same time minimizing the production of secondary waste. The process is not designed to optimize only the decontamination or only the waste production steps. It is designed to optimize the overall impact of the decontamination on each specific problem -- technologically (level of decontamination), environmentally (amount and type of waste produced), and *economically (total* cost of the decontamination and waste disposal).

Waste Production

Figure 3 provides an example of the waste volumes generated using the electrochemical regeneration mode of operation under the assumptions given in the exhibit. In this example, approximately 0.15 kg of waste is recovered electrochemically for every 1,000 kg of metal decontaminated. Those nuclides which are not electrochemically removed (Plutonium, Cerium, Cesium, and Ruthenium) are recovered through a precipitation and adsorption process (0.01 kg in the example, Fig. 3). Therefore, the total weight of the secondary waste is 0.16 kg prior to solidification and approximately double that weight, or 0.3 kg, after solidification. It is important to note that the weight added by solidification is a conservative estimate -- in practice, the amount of cement and other solidifying agents required has been found to be considerably less. In any event, this compact, minute volume of secondary waste represents the absolute minimum waste produced at today's level of understanding of contamination and decontamination problems. In the example provided in Fig. 3, the amount of secondary waste produced after solidification totals approximately 300 grams -- 0.03% of the entire steel input into the decontamination process.

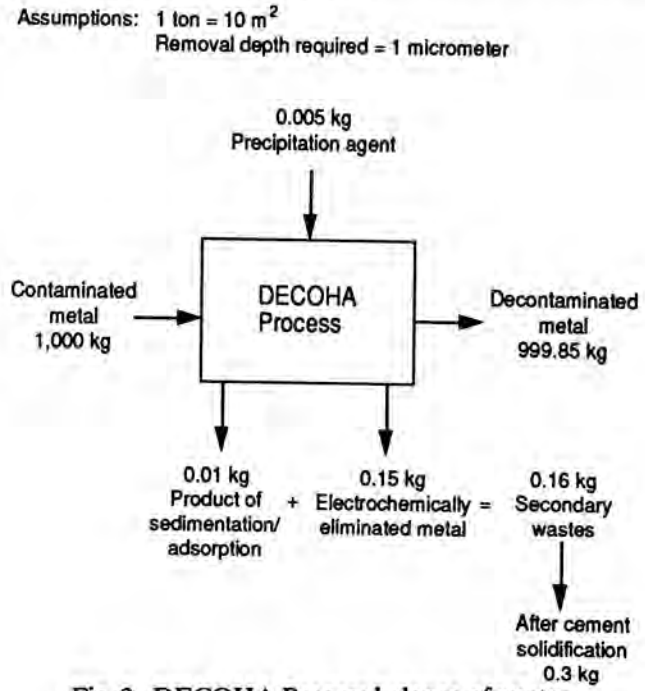

Fig. 3. DECOHA Process balance of wastes.

Changes in the waste volumes (as described in Fig. 3) may be attributed to several factors:

- An increase in the surface area of the metal per unit weight increases linearly the corresponding amount of waste produced. For example, if 1 ton of metal represents 50 m^2 rather than 10 m^2 (as assumed in Fig. 3), the amount of waste generated is 5 times greater.
- An increase in the necessary depth of removal to achieve decontamination also increases linearly the corresponding amount of waste produced. For example, if 2 micrometers of metal are removed rather

than 1 micrometer (as assumed in Fig. 3), the amount of waste generated is 2 times greater.

- The weight of oxide layers, paints, coatings, and latex layers may increase the amount of secondary waste generated.

The preceding balance of waste considers only materials used or directly involved in the decontamination and does not take into account the consumption of auxiliary aids such as gloves, paper, plastic foil, and other materials.

APPLICATION AT CHERNOBYL (3)

The DECOHA Process was selected for use at Chernobyl in order to decontaminate high-grade steel to the free limit for unrestricted use. The DECOHA plant is to be installed in an existing concrete building in the village of Dibrovo inside the 30 km zone of Chernobyl. The approximate throughput of the system is 5,000 kg of contaminated steel per day. The maximum length of the steel is 8 meters. The decontamination process consists of 6 ISO standard containers and a pumping unit. Three of these containers are used as storage and rinsing tanks for water and acid as well as to house operational plumbing (piping) and the process control equipment. The containers are built to serve as a "second containment" and each has a security basin large enough to secure the corresponding tank volumes. Since the HBF_4 dissolves nearly all metals, polypropylene (PP) was used for all key components of the plant. In instances where metal parts were necessary, these components were coated with Halar.

The plant was built in Germany and completed December 1990 -- less than one year from the start of the project planning work -- at which time it was shipped directly to the Chernobyl site. The costs for this plant, which can decontaminate 5,000 kg per day of steel in a batchwise operation, totalled roughly $1 million (excluding development work, planning, and buildings).

A simplified schematic of the DECOHA Process as applied at Chernobyl is provided in Fig. 4. This schematic indicates the basic layout for the working parts of the metal decontamination facility and shows how these components are integrated to provide the optimized decontamination and regeneration steps previously described:

- The contaminated steel is characterized (in terms of radioactivity, mechanical damage, weight, etc.) and placed in the empty decontamination cell at ambient temperature. The steel is lifted in an acid-resistant polypropylene net or basket.
- Once the decontamination basin is closed and the ventilation activated (for removal of hydrogen gas), the steel is sprayed with approximately 500 liters of "cold" (ambient temperature) HBF_4 from the small storage tanks (upper left in Fig. 4) in order to remove the loosely bound activity.
- The acid is drained or pumped from the decontamination cell back into its original storage tank (500 liters). The "used" acid (containing material and metal "debris") is continuously regenerated through a sedimentation process placed in series with the storage tank.
- The decontamination cell is then flooded with HBF_4 at 90°C (maximum) from the large storage tank (approximately 15 m^3 -- lower left in Fig. 4). The reaction is allowed to proceed for several hours at a material removal rate between 0.2 - 1.0 micrometers per hour.
- The acid solution is drained or pumped from the decontamination cell back into its original storage tank (approximately 15 m^3). This acid is continuously regenerated through electro- chemical and sedimentation processes (lower left in Fig. 4).
- The metal is then sprayed with approximately 500 liters of "cold" rinse-water from the small water-storage tanks (upper right in Fig. 4) to dilute the residual acid solution.
- This water is drained or pumped back to its original storage tanks and regenerated by means of a small distillation unit.
- The decontamination cell is flooded with rinse-water at 30°-50°C from the large water storage tank (approximately 15 m^3) shown at the lower right in Fig. 4.
- The rinse-water is then drained or pumped back into its original storage tank (approximately 15 m^3) which is operated in series with a distillation unit for continuous regeneration of the water.
- The metal, at a temperature of approximately 30°-50°C, is raised from the empty decontamination cell and transported to a shielded area for measurement to confirm that decontamination objectives have been satisfied.

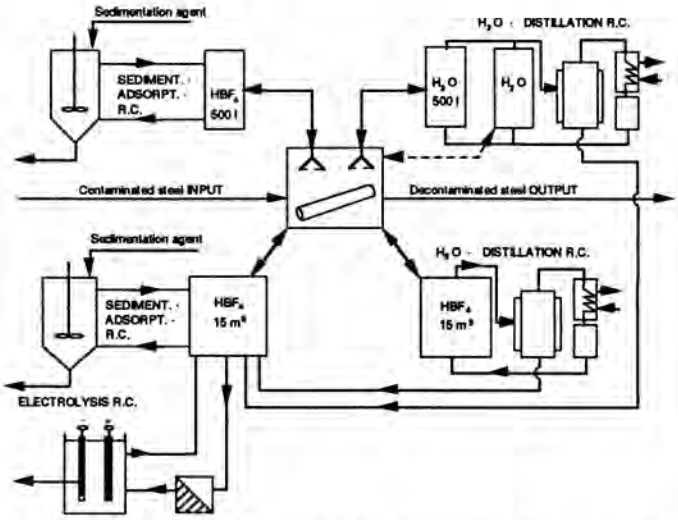

Fig. 4. DECOHA decontamination process with regeneration cycles.

- The metal is surveyed to ensure that it is free of contamination.

The plant supplied to Chernobyl offers novel possibilities for the decontamination of components and complete plant parts. Apart from the decontamination of dismantled parts, the process is also suitable for in-line decontamination of pipes and reactor components (e.g. heat exchangers, steam generators) -- thereby eliminating the need for removing such items before decontamination can take place. Plants for decommissioning entire nuclear power plants using the DECOHA Process throughout the USSR are currently being planned.

TRANSFERRING DECOHA TO ALARON

The recent broad political restructuring that has taken place throughout the USSR has delayed operation of the DECOHA Process plant at the Chernobyl site. Although delivered to the 30 km zone in February 1991, the process equipment has yet to be assembled and utilized by the responsible authorities. These events, coupled with growing interest from the nuclear industry in the United States, caused Recytec to focus its attention on market opportunities in North America. The basic reasoning behind this growing interest throughout the U.S. parallels that expressed and confirmed by the managers and engineers at Chernobyl -- the DECOHA Process provides unrivalled advantages over other decontamination technologies:

- Minimum exposure to radiation of personnel due, in large part, to the fact that the DECOHA Process requires practically no manual engagement.
- Minimum production of secondary wastes since the absolute minimum necessary surface thickness is uniformly removed from the contaminated metal surface.
- Universal applicability of the DECOHA technology for practically all metals.
- Low investment and operating costs due to the brilliantly simple concept.

In order to establish a strong foundation for growth in U.S. markets, Recytec SA Switzerland purchased Alaron Corporation during the last quarter of 1991. Alaron Corporation's fixed-base facility (NRC- regulated) in northwestern Pennsylvania and field-service capabilities nationwide provide ideal vehicles for Recytec's U.S.-targeted business ventures -- especially as a conduit for transferring the DECOHA technology into western markets.

Plans and activities are underway for adapting the Chernobyl-based design to specific decontamination opportunities within Alaron's current base of projects and customers. In addition, recent results with a modified version of the DECOHA Process have proven highly successful in the decontamination of lead (Pb) and lead-shielding materials (4,5). Testing activities are currently underway at Alaron and an industrial-scale DECOHA Process facility is planned for start-up later this year.

REFERENCES

1. J. HANULIK, Process For Decontaminating Radioactively Contaminated Metallic Materials. United States Patent, Patent Number 4,828,759 (May 9, 1989).
2. J. HANULIK, Dekontamination von radioaktiv kontaminierten Oberflachen. Doctoral dissertation Nr. 9460 at the Swiss Federal University of Technology, Zurich, Switzerland, under Prof. Dr. D.W.T. Rippin (May 1991).
3. H.W. BEAUJEAN, J. FIALA-GOLDIGER, and J. HANULIK, "DECOHA at Chernobyl," Nuclear Engineering International (April 1991).
4. J. HANULIK and J.F. EQUEY, Reagent for Dissolving Radioactively Contaminated Surfaces from Metal Articles, Patents Pending.
5. J. HANULIK and J.F. EQUEY, Method for Dissolving Radioactively Contaminated Surfaces from Metal Articles, Patents Pending.