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DEVELOPMENT OF A CLEANING PROCESS FOR URANIUM CHIPS MACHINED WITH A GLYCOL-WATER-BORAX COOLANT

P. A. Taylor

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P. A. Taylor

Chemical Engineering Department

Y-12 Development Division

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Oak Ridge Y-12 Plant
P.O. Box Y, Oak Ridge, Tennessee 37831

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CONTENTS

SUMMARY

A chip-cleaning process has been developed to remove the new glycol-water-borax coolant from oralloy chips. The process involves storing the freshly cut chips in Freon-TDF until they are cleaned, washing with water, and displacing the water with Freon-TDF. The wash water can be reused many times and still yield clean chips and then be added to the coolant to make up for evaporative losses. The Freon-TDF will be recycled by evaporation. The cleaning facility is currently being designed and should be operational by April 1985.

INTRODUCTION

A new water-based coolant has been developed to replace the current perchloroethylene-mineral oil coolant in the oralloy machine shop. The coolant consists of 90 g/L borax and 1000 mg/L nitrite (NO_2^-) in a 50-50 solution of propylene glycol and water. A new cleaning process was required to remove the glycol and borax from the oralloy machine turnings (chips).

Initially, it was planned to store the chips in coolant until they were washed. The corrosion rate of uranium specimens in the new coolant was less than 2 µm/year, so it was expected that the chips could be stored in coolant for extended periods of time without any adverse effects. However, an oxide layer was rapidly formed on the chips, and this oxide layer chemically trapped boron on the chips (Fig. 1). The only method found to remove this chemisorbed boron was to dissolve the oxide off the chips.

A chip-cleaning process was developed using a dilute solution of sodium carbonate and hydrogen peroxide to remove the oxide layer. However, this process was complicated and would have been very expensive to build and operate. It was later found that an alternate storage media, Freon-TF* (trichlorotrifluoroethane), prevented the formation of the oxide layer. Freon-TF displaces most of the coolant from the chips, preventing the coolant from significantly oxidizing the chips. Adding a proprietary surfactant to the Freon-TF increases the efficiency of the coolant displacement by at least an order of magnitude.

The chip-cleaning process consists of washing the chips in water and then displacing the water with Freon containing a surfactant. Both operations are carried out in an ultrasonic tank. Two ultrasonic units were used in the development of the process; a pilot-plant cleaner used to wash depleted uranium chips and a prototype unit used on oralloy chips.

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*E.I. DuPont De Nemours & Co., Inc., Wilmington, DE.

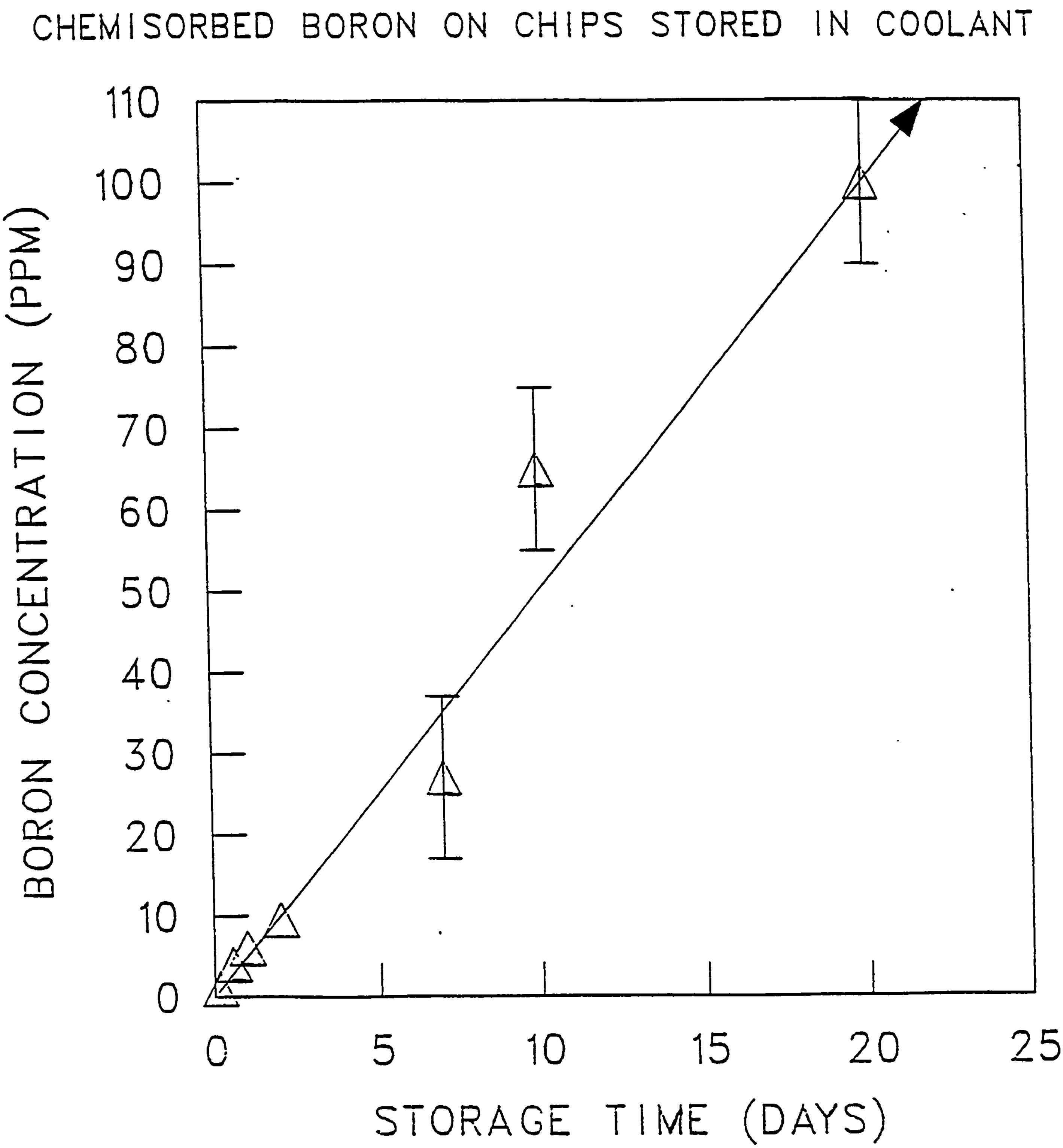

FIG. 1. CHEMISORBED BORON CONCENTRATION ON URANIUM CHIPS STORED IN GLYCOL-WATER-BORAX COOLANT

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PRESENTATION OF EXPERIMENTAL RESULTS

EQUIPMENT

The pilot-plant chip-washing facility consists of a cylindrical ultrasonic washing module 15 cm I.D. by 100 cm tall. The module is powered by six 1 kW generators at a frequency of 20 KHz. The wash module holds about 20 L of liquid. The prototype unit is similar, except that the wash module is 14 cm I.D. and holds 15 L of liquid. The uranium chips are handled in stainless steel baskets 11.4 cm O.D. by 90 cm tall, with a wall thickness of 0.15 cm.

CLEANING PROCEDURE

Uranium chips are cut using the new coolant and then placed inside a chip basket and covered with Freon-TDF (Freon-TF + ∿100 ppm surfactant). The surfactant is a quaternary ammonium phosphate ester. Each basket of chips is washed in water for 2 min using ultrasonics, and then the water is displaced using Freon-TDF. The ultrasonic cycle for the Freon-TDF rinse is two 1-min power cycles, each followed by a 5-min soak to allow the displaced water to float to the top. The water is skimmed off the top of the Freon-TDF, and then the basket of chips is sampled. In the production process, the complete cleaning process will be repeated a second time, and then the basket of chips will be stored in clean Freon-TDF prior to drying in warm argon, briquetting, and casting.

BORON BUILDUP

In the production chip-cleaning operation, each batch of wash water will be used to clean many baskets of chips. The concentration of coolant and surfactant in the wash water will slowly increase. The increase in boron (from the coolant) and phosphorus (from the surfactant) in the wash water was measured using the pilot-plant cleaner. Eight baskets of chips were washed and the boron and phosphorus concentration in the wash water was measured after each basket. Water was added to the cleaner as needed to replace the water retained on the chips, an average of 400 mL/basket. The phosphorus concentration increased to 0.4 mg/L after four baskets and then remained constant. The boron concentration is shown in Fig. 2 (Line A).

Boron buildup in the wash water was also measured using the prototype facility. Figure 2 (Line B) shows the increase in boron concentration for 22 baskets of oralloy chips. The boron buildup was more rapid in the prototype cleaner because of the smaller initial water volume (15 L vs 20 L) and the lower makeup water requirements. Figure 3 shows that there is a good correlation between conductivity and boron concentration in the wash water. The production chip-washing facility will have conductivity meters to monitor the wash water. A boron concentration of 1000 mg/L in the wash water would leave about 0.5 ppm boron on the chips since the Freon-TDF rinse leaves only about 500 ppm of the wash water on the chips.

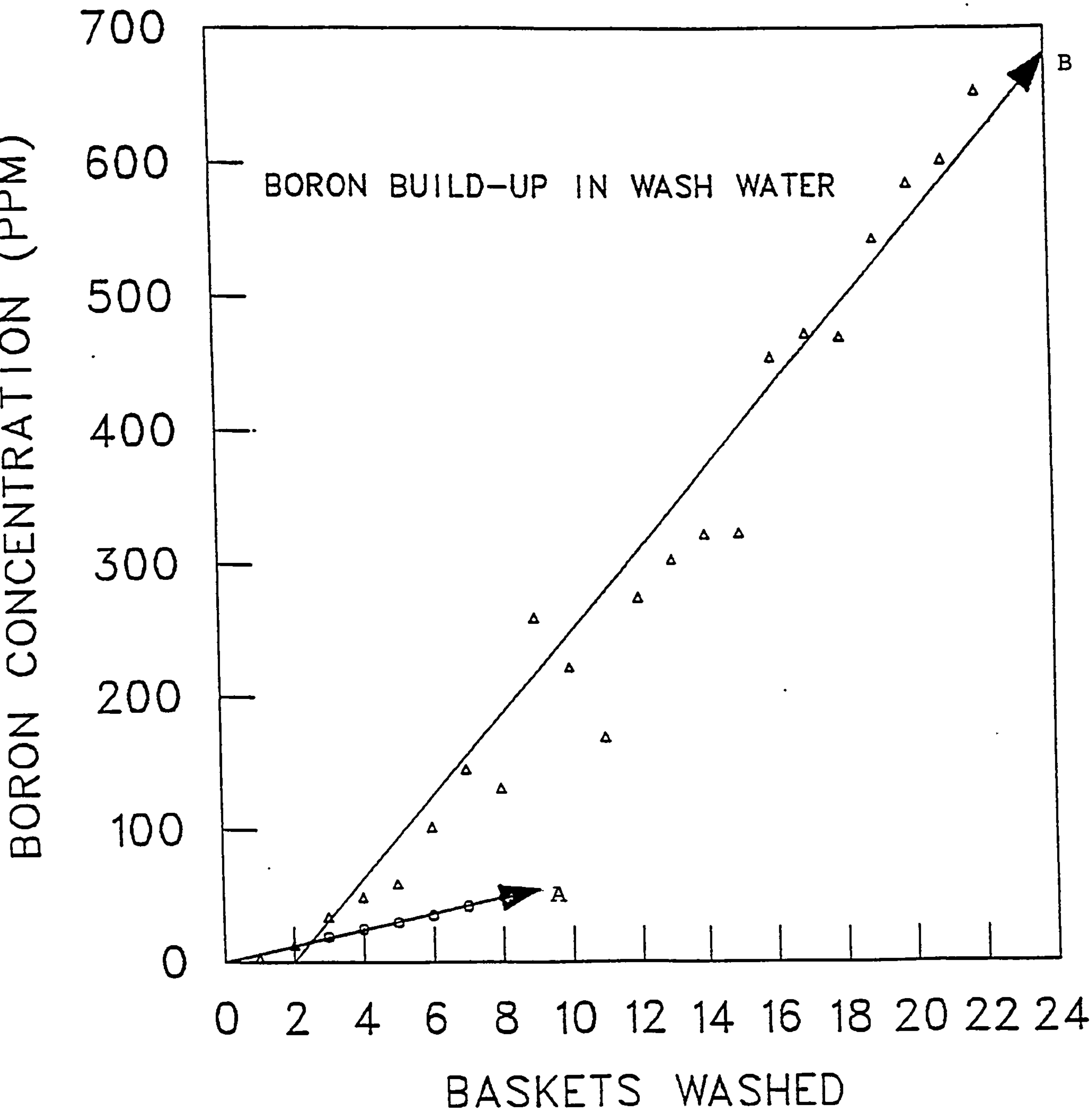

FIG. 2. BORON CONCENTRATION IN WASH WATER
A - PILOT-PLANT CLEANER, 400 mL/BASKET MAKEUP WATER
B - PROTOTYPE CLEANER, 110 mL/BASKET MAKEUP WATER

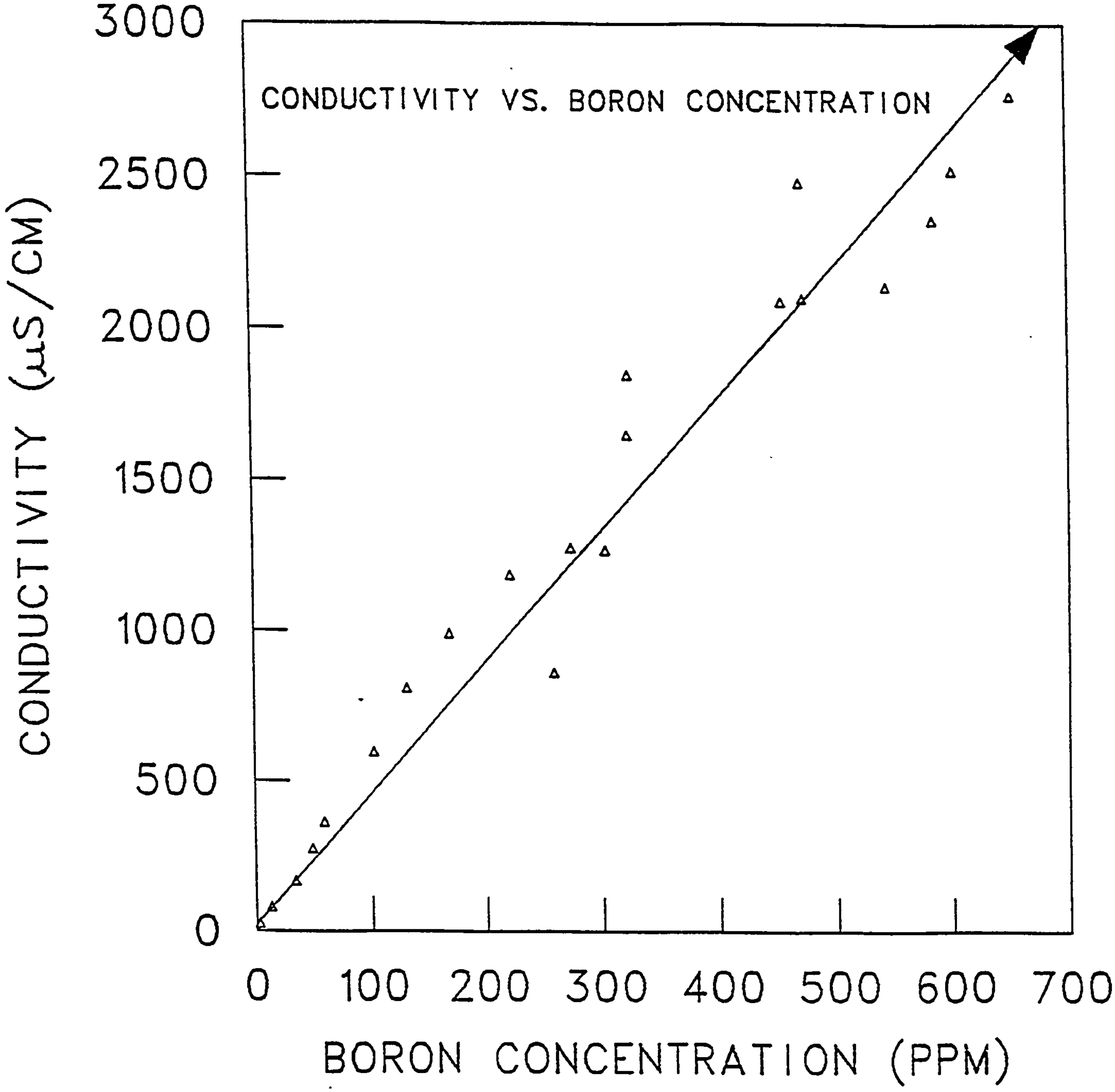

FIG. 3. CONDUCTIVITY VS BORON CONCENTRATION IN WASH WATER

TEMPERATURE BUILDUP

The energy imparted by the ultrasonic transducers increases the temperature of the fluid inside the ultrasonic cleaner. The temperature rise was measured in the pilot-plant cleaner for both water and Freon-TDF. The pilot-plant cleaner has 6 kW of total ultrasonic power and holds 20 L of liquid.

When filled with water, the temperature increases an average of 4°C for a 2-min ultrasonic cycle. Freon-TDF increases an average of 7°C for a 1-min cycle.

EXTENDED STORAGE TIME

Several baskets of depleted uranium chips were stored in Freon-TDF for up to 35 days before washing. The chips were still bright and shiny without any visible sign of corrosion. The boron concentration on the washed chips increased from 1 ppm after 7 days to 4 ppm after 21 and 35 days storage in Freon-TDF.

Several baskets of chips were washed once and then dipped in coolant and placed back in Freon-TDF for later use. There was a light layer of oxide on the chips after 3 days storage and a fairly heavy oxide layer after 12 days. Baskets that were rewashed after three days showed an increase in the amount of water left on the chips after the Freon-TDF rinse, but no significant increase in boron concentration. The chips stored for 12 days showed increases in both water and boron levels after washing. Further tests are in progress to understand this phenomenon, although it does not have any apparent impact on the proposed chips-washing process, since cleaned chips will not be in contact with coolant.

SURFACTANT

Freon-TDF contains about 100 ppm of a quaternary ammonium phosphate ester dissolved in toluene. The formula for the surfactant is $(C_{12}H_{25})_2 N^+(CH_3)_2PO_2^-(OH)_{0.5}(OC_8H_{17})_{1.5}$. The toluene is 50 wt% of the surfactant mixture that is added to the Freon. In the production process, the Freon-TDF will be reclaimed by a single-stage evaporation process. The surfactant and most of the toluene will be left in the residue. It will be necessary to add 15.1 vol% Freon-TDFC (660 ppm surfactant) to the reclaimed Freon to restore the original surfactant concentration. A small amount of toluene will evaporate along with the Freon, but since there is not an azeotrope formed between the two, there should not be a long-term buildup of toluene.*

The surfactant is very effective in reducing the surface tension of water, thus allowing the Freon to more efficiently displace the water. Various concentrations of surfactant in Freon were tested in laboratory-scale experiments for water removal from uranium chips. The results of these tests are shown in Table 1.

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*DuPont Production Information Center.

Table 1

EFFECT OF SURFACTANT ON WATER REMOVAL FROM CHIPS

Surfactant Concentration (ppm)	Residual Water on Chips (ppm)
0	41,000
20	12,200
40	4,020
80	3,100
120	3,000
660	1,920

The prototype wash unit yielded residual water levels of less than 500 ppm using 80 ppm surfactant.

In the production process, there are three different mechanisms for losing surfactant from the Freon; it can be absorbed on the surface of the chips or extracted by water or coolant.

Freon-TDF will contact coolant in the stainless steel cans used to store chips in the machining area and in the transport dollies. The coolant will be skimmed from the top of the Freon-TDF and returned to the coolant system. The analytical techniques available were not sensitive enough to measure the distribution coefficient for surfactant between coolant and Freon-TDF. One test using Freon-TDFC (660 ppm surfactant) in contact with an equal volume of coolant gave a distribution coefficient of 200, which if confirmed, means that most of the surfactant extracted into the coolant. In the production process, the volume of coolant contacting the Freon-TDF will be relatively low, which will reduce the amount of surfactant removed.

Freon-TDF will contact water and chips in the cleaning process. The distribution coefficient for surfactant between water and Freon-TDF is about 0.2. In the production process, 15 L of Freon-TDF will contact about 400 mL of water for each basket of chips cleaned, so less than 1% of the surfactant originally present in the Freon will be removed by the water for each basket of chips.

The main pathway for surfactant loss will be that carried out on the chips. Surfactant concentration on the chips has averaged 40 ± 20 ppm (∿1 ppm phosphorus). For a basket containing 3 kg of chips in contact with 15 L of Freon-TDF, the chips will remove about 10% of the surfactant from the Freon-TDF.

During the oralloy chip-cleaning tests using the prototype facility, a total of 22 baskets of chips were treated using one 30-L batch of Freon-TDF. The water concentration on the chips after the Freon-TDF rinse averaged less than 300 ppm. The water content of the later baskets was not significantly higher than for the earlier ones, so the surfactant was still effective.

BASKET LOADING

During the oralloy tests, the amount of chips in each basket was limited to below 3 kg. Increasing the chip loading would decrease production costs. Baskets of chips with various amounts of uranium were washed in the pilot-plant facility, and boron concentration left on the chips was compared. There was not any increase in residual boron levels as the chip basket loading was increased from 2.5 kg to 3.6 kg.

SURFACE CHIPS

Most of the uranium chips used in the development tests were cut from large castings of uranium and did not have any oxide layer on the chips. To determine if a previously formed oxide layer would effect the chips cleaning efficiency, four baskets containing oxided chips were washed. Each basket contained about 1/4 surface-cut chips from as-cast rods, with the remainder of the chips being interior cuts. Both types of chips were sampled from each basket. There was not a significant difference in the boron level of the two types of chips. The presence of an oxide layer prior to the chips contacting coolant does not result in a significant amount of chemisorbed boron.

CONCLUSIONS

The proposed chip-cleaning process will produce clean, dry oralloy chips for recycle. The wash water can be reused extensively and then added to the coolant as makeup for evaporative water losses. The Freon-TDF will be recycled by evaporation to remove oil and dirt and then restored to the proper surfactant concentration by adding Freon-TDFC. The design and operating parameters for the new chip-washing facility have been determined.

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