DECONTAMINATION AND DECOMMISSIONING OF A PLANT FOR THE URANIUM RECOVERY FROM WET-PROCESS PHOSPHORIC ACID

Da-Ping Wang, Ben-Li Pen, and Ying-Chu Hoh
Institute of Nuclear Energy Research
Lung-Tan Taiwan, Republic of China

ABSTRACT

Decontamination and decommissioning (D&D) of a plant for the recovery of uranium from wet-process phosphoric acid plant was achieved in the last two years. Five-stage plan was proposed for D&D. There were (1) over-all survey for the whole plant and its environment, (2) D&D plans for safety review, (3) removal chemicals, area classification and D&D for the facilities, (4) waste treatment, collection and packaging, (5) FSAR and follow-up survey for the plant and its environment. The D&D plans were included operation procedures, radiation safety analysis, and PSAR etc. During decontamination, radioactivity less than 370 Bq/g or the removable contamination $\alpha < 0.5$ Bq/100 cm^2 and $\beta + r < 5$ Bq/100 cm^2 were regarded to non-radioactive material and was treated by EPA regulations. The chemicals used were nitric acid, ST-KON, TURCO-5315 and 4215. After decontamination, all of the surveillance results of URPA plant meet the regulations, but in order to ensure the safety, the facilities were restricted to remain in the plant.

INTRODUCTION

In 1977, the Institute of Nuclear Energy Research (INER) of the Republic of China (ROC) started to study the process to recover uranium from wet-process phosphoric acid (URPA). Due to the high price of uranium at that time, in 1981, a production plant based on D2T-D2D (1) process with a capacity of 10 tons of yellow cake per year was finished and operated.

Since 1987, the plant for the recovery of uranium from wet phosphoric acid has been getting harder and harder to operate due to an uneconomic results. In 1986, the institute even did a critical review on the plant, both technically and economically. The results were (1) technically, the institute has gained a fruitful experiences and process know-how for such a plant, and (2) economically, because the price of uranium has fallen, the plant was totally uneconomic from the price point of view. Therefore, a recommendation to decontaminate and decommission(D&D) the plant was proposed by the review team.

In 1988, a D&D team was formed and started to plan. The D&D planning and operation must meet the regulations of Atomic Energy Council (AEC), and Environmental Protection Administration (EPA). Five-stage plan was proposed by the D&D group, there were (1) over-all survey of the plant and its environment, (2) preliminary safety analysis report (PSAR) and D&D plans for safety review, (3) area classification, chemical removal and facilities D&D, (4) wastes collection, classification and packing, and (5) final safety analysis report (FSAR) and follow-up survey for the plant and its environment periodically.

URPA PLANT

Figure 1 shows the block diagram of the D2T-D2D process for the recovery of uranium from wet-process phosphoric acid. The process contained pretreatment, post-treatment, two extraction cycles, ammonium uranyl tricarbonate (AUT) precipitation and filtration. The organic extractant used in the first and second extraction cycles were di(2-ethylhexyl) phosphoric acid (D2EHPA) mixed with trioctyl phosphine oxide (TOPO) and D2EHPA mixed with dibutylbutyl phosphonate (DBBP), respectively. The uranium content in the phosphoric acid was approximately 80 PPM. After the first extraction cycle, the uranium content was upgrade to 7 g/l. While in the second cycle, uranium was kept in a saturation level until the products formed. The over-all through-puts from the first and second cycle were 20 M^3/hr and 0.15 M^3/hr. The whole plant was divided into five areas,i.e. (1) wet-process phosphoric acid pretreatment, (2) the first extraction cycle, (3) the second extraction cycle, (4)post-treatment and (5) uranium precipitation area. Figure 2 shows the plant overview. The mixer-settler used in the first extraction cycle with a dimension of 7.1 x 1.5 x 1.6 M was fabricated by FRP. Figure 3 shows the overview of first extraction cycle.

DECONTAMINATION AND DECOMMISSIONING REGULATIONS

For the pretreatment, post-treatment and the first extraction steps, the uranium contents were below the nuclear material control limits. Those areas were treatment as a chemical plant and EPA regulations were applied. For the stripping step of the first extraction cycle together with the second cycle, the uranium contents were higher than 7 g/l, the following Acts and regulations of ROC and INER were applied.

1. Detailed Regulations for Implementation of the Atomic Energy Law,
2. Standards for the Protection Against Ionizing Radiation,
3. The Safety Rules for Transportation of Radiation Materials,
4. NRC Regulation Guide 1.86 Table 1.,

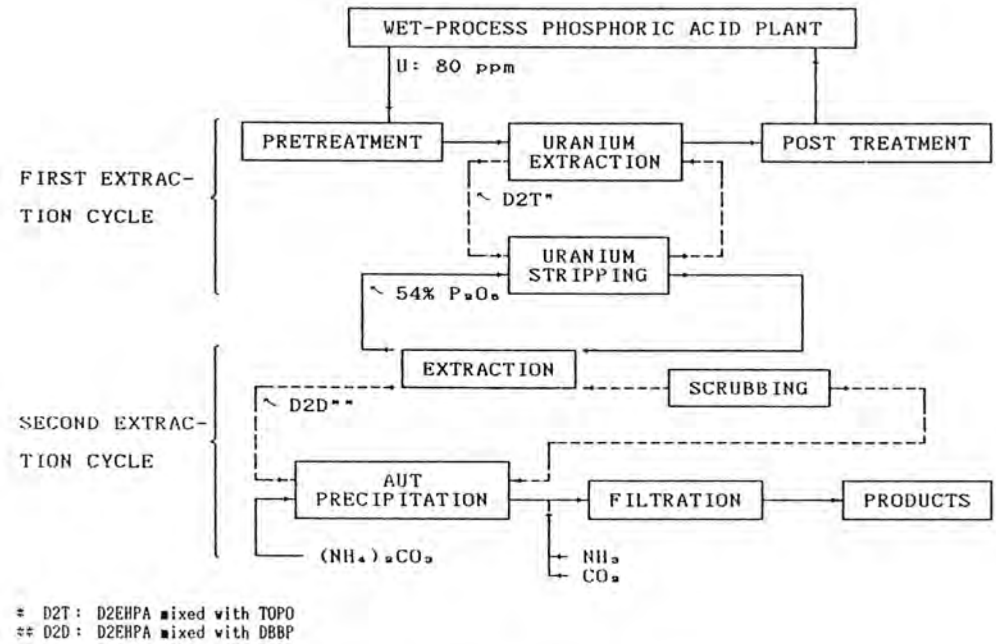

Fig. 1. Block diagram of URPA process.

Fig. 2. An over view of URPA plant.

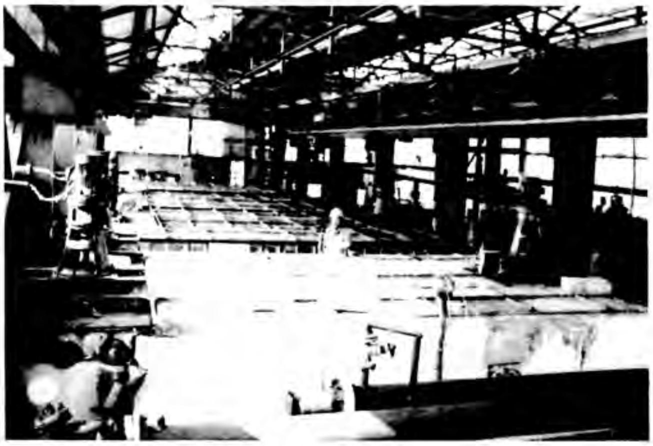

Fig. 3. An over view of the first extraction cycle.

5. The Rules of Radiation Protection for Worker of INER,
6. The Acceptance Criteria for Radwaste of INER, and
7. The Rules for Radwaste Controlled and Treatment of INER.

Apart from the above acts as well as the regulations, as low as reasonably achievable (ALARA) was also followed strictly.

Based on the above acts as well as regulations, the following standards were adopted:

1. The liquid wastes can be treated as chemical wastes when the natural uranium content in the waste was less than 0.222 Bq/ml (8 μg/ml). The total amount should not exceed 1 kg/yr. However, EPA regulations were applied.
2. The solid wastes can be treated as an ordinary wastes when the solid radiation specific activity was less than 74 Bq/g. The total amount should not exceed 1 kg/yr. EPA regulations still applied.
3. Same as the No. 2 standard when the nature uranium radiation specific activity was less than 370 Bq/g.
4. The solid wastes with surface dosage between 10^{-5} - 5×10^{-4} Sv/hr were shipped back to the radwaste treatment plant of INER for the further treatment.
5. The solid wastes with surface dosage rate ranged from 5×10^{-4} - 0.02 Sv/hr were decontaminated first. After its dose rate down to 10^{-5} - 5×10^{-4} Sv/hr, those wastes were treated as described above.

The facility decontamination was divided into two categories, the inside of the systems, i.e. the inside of the equipment, piping, valves, etc., were treated as a green area, the outside of the systems was white area. Each of them for the removable contamination has the following decontamination standards.

1. For the outside surface of equipment, the removable contamination limit: α < 0.5 Bq/100cm^2, β/r < 5 Bq/100cm^2, dose rate limit: < 2.5×10^{-6} Sv/hr
2. For the inside surface of equipment, the removable contamination limit: α < 2 Bq/100cm^2, β/r < 20 Bq/100cm^2, dose rate limit: < 2.5×10^{-5} Sv/hr

TABLE I

Average Dose Rate for Equipment and Areas

Equipment or Area	Survey Reading, β, r (10^{-5} Sv/hr)	Smear Test (Bq/100cm^2) α	β
Outside Surface of 1st Extraction Equipment	0.14	0.30	0.95
Outside Surface of 1st Stripping Equipment	0.1	0.12	0.62
Outside Surface of 2nd Extraction Equip.	0.27	11.36	36.65
AUT Precipitator	1.31	46.70	180.0
Ground of Control Room	<0.06	0.84	2.0
Ground of Tank Farm	<0.06	0.22	0.3
Grid Plate of 2nd Fl.	0.06	1.06	2.06
Wall of Office Bldg.	<0.04	0.09	0.18
Roads, Outside of Plant Bldg.	<0.04	0.05	0.11

TABLE II

Average Uranium Content of Deposited Gypsum in Individual Equipment

Equipment	Uranium Content ($\mu g/g$)
Acid Tanks of Pretreatment	30
Mixer-Settlers In 1st Extraction	123
Mixer-Settlers In 1st Stripping	2352
Inclined Plate Organic Separator	91
Air Purged Organic Separator	82
Equipment in 2nd Cycle	> 8600

Fig. 4. Radioactive surveillance for the whole plant.

Fig. 5. Solid waste shipped back to INER.

OVER-ALL SURVEY OF THE PLANT AND ITS ENVIRONMENT

Radioactive surveillance including the plant and its environment was executed by health physics people as shown in Fig. 4. The estimations of the contamination level were based on Geiger survey meter readings together with surface smear tests. The only contaminant was nature uranium which was deposited on the surface of equipment, piping, valves, tanks, etc. Table I summarized the results of radioactive surveillance of the plant. It indicated that the most contaminated areas were the AUT precipitation step and the second extraction cycle. Table II showed the uranium content in gypsum which was deposited inside the equipment.

From the regulations, only the specific activity greater than 370 Bq/g or the surface dose rate greater than 10^{-6} mR/hr (10 cm distance) were considered as a radioactive waste. Based on the above regulation along with Table I and II, the areas need to decontaminate were (1) the stripping equipment of the first cycle (2) the second cycle (3) the AUT production area and (4) the slightly contaminated extraction equipment of the first cycle. And all of the gypsum should be collected, packed and shipped back to INER for the further treatment.

DECONTAMINATION AND DECOMMISSIONING PLAN

A decontamination and decommissioning plan was prepared for nuclear safety review before the D & D works proceeded. The plan included:

1. The plant shut-down operation and D&D planning,
2. Work break-down structure schedule,
3. The proposed Acts and regulations,
4. The plant and its environment survey,
5. Area classification
6. Residual materials removal,
7. Equipment clean up,
8. PSAR and environment assessment reports,
9. Decontamination operation,
10. Waste treatment plan, AND
11. Property transfer to acid plant.

The proposed criteria for decontamination were the radioactivity less than 370 Bq/g or α and/or $\beta+r$ surface dose rate less than 0.5 and/or 5 Bq/100cm^2 were regarded as non-radioactive material. However, the EPA regulations were applied. The decontamination and dismantle procedures were included in the PSAR.

CHEMICAL REMOVAL AND DECONTAMINATION AND DECOMMISSIONING OF THE PLANT

As mentioned previously, the most contaminated areas were the second cycle and the precipitation step. The stripping of the first cycle was also contaminated but slighted. The chemicals needed to remove were phosphoric acid, extractant, and ammonia carbonate pregnant with uranium. Phosphoric acid was returned to the acid plant through the oil separator to remove the trace amount of the organic entrainment. Part of the extractant which contained 25 ppm of uranium was treated by an organic polar solvent to recover D2EHPA, TOPO and kerosene separately with a novel technology (2). This technology was developed by INER. The other extractant was mixed with large amount of crude oil for oil refinement. The ammonium carbonate solution contained 4 g/l of uranium. Carbon dioxide and ammonia were introduced in order to precipitate the uranium content. After filtration, the filtrate was concentrated by vacuum distillation, the concentrate was collected and shipped back to INER for the solidification treatment.

TABLE III

The Quantity of Agents Used for Decontamination

Agent	Quantity (M^3)
2N Nitric Acid	0.02
ST-KON	0.08
Turco-5315	0.01
Turco- 4215	0.01
Waste Water	50.0

Fig. 6. AUT Crystallizer after D&D.

Most of the equipment of the plant was below the contaminated limits, those equipment were treated by ordinary procedures with the application of EPA regulations. Before decontamination, the dust deposited on the outside surface of the equipment was cleaned by vacuum cleaner and the metal part was painted after cleaning. The disassembled parts were treated very carefully. High pressure water jet was used to clean the surface of the equipment. The used water collection system was equipped in order to collect the waste water. Nitric acid, ST-KON, TURCO-5315 and 4215 (products of PUREX Co. USA) were used as the decontamination agents. The gypsum deposited on the mixer settlers and other equipment were removed by hand tools. Figure 5 showed the solid wastes which generated during decontamination were shipped back to INER. In order to reduce the amount of liquid waste, Table III showed the minimized amount of the decontamination agent used.

After decontamination, solid wastes with an amount of 22 drums of 200 Liter were collected and shipped back to INER for the further treatment. The collected liquid wastes were sent to the waste treatment facilities of the acid plant. After treatment, the wastes were monitored before discharging. Table IV indicated that after decontamination, the radiation distribution was well below the limits. Figure

6 showed the AUT products crystallizer after decontamination.

FINAL SAFETY ANALYSIS REPORT AND FOLLOW UP SURVEY

The FSAR of this case was a decontamination and decommissioning. Hence, it was emphasized the very low radiation effect of the URPA plant on the future workers and the environment. The exposure possibility as well as the pathway to human body and environment were studied seriously and carefully. The results indicated that for 2000 working hours per year, the dose rate per worker exposure was 1.45×10^{-7} Sv/yr (3) and this was far below the regulation limit. However, in order to protect environment and other area's workers, a rigid limitation was proposed to prohibit any removal of the equipment from URPA plant to the outside of the building or other areas.

Several thermo luminescent dosimeter (TLD) dection points were selected in order to protect the environment from contamination. The TLD and waste water samples were collected and analyzed every two months. The results indicated that the plant and its environment are in good condition.

CONCLUSION

The decontamination and decommissioning of the plant to recover uranium from wet-process phosphoric acid was possibly the first case in the world. The experiences and technology were worth reporting. Although it was a nature uranium case, the institute still treated it very seriously and carefully for the safety of environmental protection.

During D&D operation, ALARA has to be followed strictly. The set-up of the reasonable regulations were also a difficult problem. During decontamination the waste water has to be control strictly in order to prevent the secondary contamination, solid wastes has to record correctly before sent to the other area, decontamination agents has to minimize the variation and amount used. The only deep regret was that the compositions of some commercial decontamination agents were unknown due to their commercial benefits.

REFERENCES

1. Hsiao-Ming Chen, Haw-Jan Chen, Ying-Ming Tsai, Te-Wei Lee, Gann Ting " Development of an improved two-cycle process for recovering uranium from wet-process phosphoric acid " Ind. Eng. Chem. Res., Vol. 26, No. 3, 1987
2. B.L Pen, D.P Wang, Y.C Hoh, K. H Tsao " A new process for the recovery of extractant from extraction solvent " patent pending, 1990.
3. P.T Lee, T.H Wong " Analysis the very low radiation effects for URPA facilities " Group report, Sep. 1989.

TABLE IV

Average Dose Rate for Equipment and Areas after Decontamination

Equipment or Area	Smear after Decontamination		Smear after Decontamination and Painted *	
	α	β	α	β
Mixer-Settlers	0.23	0.43	-	-
Outside Surface of Equipment	0.08	0.42	-	-
Steel Structure	0.17	0.28	LLD**	LLD
Ground of Plant	0.17	0.32	-	-
Outside Surface of Piping, Pumps	0.17	0.38	LLD	LLD
AUT Precipitator	0.33	0.71	-	-

* Removable Contamination Unit: Bq/100cm^2
** LLD: Low Limited Detection