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DISPOSAL OF LOW-LEVEL RADIOACTIVE WASTES FROM PILOT PLANT OPERATIONS

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ABSTRACT

Pilot Plant operations at the National Lead Company of Ohio include the solvent extraction of thorium, the testing of new methods for thorium metal production, and various operations with uranium materials. Most liquid wastes from these operations are given local treatment and then sent to a central facility for additional treatment. Neutralized wastes with no scrap value are then sent to a settling basin. Clear effluent from the basin is discharged to the Great Miami River.

Residues from acid-digestion processes may be drummed for later uranium or thorium recovery. Most solid waste is sent to on-site disposal pits; however, certain thorium residues are drummed for disposal at an off-site commercial burial ground.

INTRODUCTION

The National Lead Company of Ohio produces uranium and thorium materials for the Atomic Energy Commission. The major product is uranium metal for AEC reactors. Production begins with feeds of various types and purities from other sites. Solvent extraction of the uranium may be carried out for additional purification. The extraction product, an acidic solution of uranyl nitrate hexahydrate, is converted to uranium trioxide, an orange powder called "orange oxide." The UO_3 is reduced by hot hydrogen to UO_2, and the UO_2 is reacted with anhydrous hydrogen fluoride to form uranium tetrafluoride, commonly called "green salt." Uranium reguli are produced by reacting UF_4 and magnesium metal in a reduction vessel. The reguli are remelted under vacuum to produce a uranium ingot which is then rolled into rods. Blanks are cut from the rods and then machined to final dimensions. The final metal product is a fuel element core.

Various forms of thorium have also been produced. These products have included (1) acid solutions of thorium nitrate tetrahydrate (2) thorium hydroxide gel and powder (3) thorium tetrafluoride (4) thorium oxalate and (5) thorium metal.

PILOT PLANT

Activities in the Pilot Plant have included experimental pilot operations and tonnage quantity production of both thorium and uranium materials. At present, a major activity is the production of thorium metal, using new processes. The handling of wastes from this and other Pilot Plant operations will be the major subjects of this paper.

The main Pilot Plant building covers about 23,000 square feet. The entire complex consisting of the main building, storage pads, and tanks covers about 100,000 square feet. Major equipment includes a solvent extraction system; a so-called "wet area" for aqueous feed dissolution and precipitation steps; and a "dry area" which contains furnaces, heat treating systems, and other equipment for metal production. These operations produce several waste streams, all of which contain low levels of radioactivity.

THORIUM REFINING

Feed material for the Pilot Plant thorium operations consists primarily of thorium nitrate tetrahydrate, $Th(NO_3)_4 \cdot 4H_2O$, and thorium dioxide. Solids which are readily soluble are dissolved without added heat in 5 N nitric acid. Less soluble feeds are digested at 230° F in 12 N nitric acid. A small amount of hydrofluoric acid is added, if needed, to catalyze the reaction. After digestion, the prepared solution is filtered through a cartridge filter or a plate-and-frame filter.

Another major source of feed is thorium which has been reprocessed after irradiation in a nuclear reactor. It is received as a semi-purified thorium nitrate solution. For extraction feed it is adjusted to the proper concentration of nitric acid and thorium, and then filtered through a cartridge filter.

Thorium is separated from the remaining impurities in the feed solution by solvent extraction in a series of pulse columns (see Figure 1).[1,2] In the first column, the thorium nitrate feed solution is mixed with an organic solvent (30% diamylamyl phosphonate (DAAP) and 70%

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Solvesso-100). In the second column, the thorium-laden organic phase is scrubbed with deionized water to aid in the removal of impurities. In the third column, the scrubbed organic is mixed with dilute nitric acid which re-extracts the thorium. This aqueous phase, which now contains the thorium, is then passed through a cartridge filter and transferred to a steam-heated boildown tank. Heating is continued until the desired thorium concentration is achieved. If uranium was present in the feed, this concentrated solution is passed through a second extraction system to remove it (see Figure 2). The uranium extractant is an organic solvent consisting of 12% tributyl phosphate, 30% Solvesso-100, and 58% kerosene. After extraction, the TBP solution is mixed with water to strip the uranium and the small amount of thorium which is also extracted. This strip solution is reduced in volume by heating to increase the thorium concentration from 20 g/l to 400 g/l. When enough of this concentrated strip solution has been accumulated, it is recycled through the extraction system for uranium removal and recovery of thorium.

PRECIPITATION OF ThF_4

Purified thorium nitrate solution is used as the feed for the production of ThF_4. Hydrofluoric acid is added to the thorium nitrate solution in a polypropylene tank. Thorium tetrafluoride is precipitated and collected in a box filter. The washed damp cake is scooped from the filter into stainless steel pans and then oven-dried. The ThF_4 is subsequently calcined at 1000° F in an Inconel retort. During calcining, the retort is purged with a nitrogen-HF stream.

REDUCTION OF ThF_4 TO THORIUM METAL

In the production of thorium metal, calcined ThF_4 and a zinc halide are blended with calcium metal and the mixture is placed in a steel furnace vessel with a refractory liner. The charge is heated until a thermite-type reaction occurs, reducing the ThF_4 and zinc halide to a Th-Zn alloy and converting the calcium metal to a calcium halide slag. The Th-Zn regulus is then heated under vacuum to vaporize the zinc. Final product is a dense thorium metal sponge.

WASTE TREATMENT

Aqueous effluents are the major type of contaminated waste from the thorium operations described in the preceding section. Treatment of these effluents is required for one or more of the following reasons:

1. An effluent may contain enough thorium to make recovery economical.
2. Radioactive daughter products of thorium may be present in sufficient quantity to require removal so that the combined plant effluent meets requirements for release to the Great Miami River.
3. Acid solutions require neutralization before being sent to the central waste handling facility for additional treatment and disposal.

Effluents from certain processes, such as thorium extraction,

are transferred to hold tanks and receive specific treatment. Other liquid wastes and floor washings drain into floor trenches and below-ground sumps. From these sumps, the wastes are pumped to above-ground accumulator tanks and then treated for material recovery or for disposal.

EXTRACTION WASTE

The extraction process produces as much as 1500 gallons per day of an acidic waste called "extraction raffinate." This raffinate is what remains of the feed solution after the thorium has been extracted. It contains about 2 N nitric acid and most of the impurities originally present in the feed solution: sodium, calcium, sulfate, fluoride, rare earths, iron, etc. It also contains the radioactive decay products of thorium. Treatment is aimed at neutralizing the acid and reducing the amount of radium-228, a radioactive daughter product of thorium. Radium-228 is a beta emitter with a 6.7 year half-life and has a low permissible level in drinking water. Its concentration in the waste solution is controlled to prevent its reaching water supplies via the Great Miami River. The radium-228 is removed by coprecipitation with barium sulfate. Decontamination is improved by the formation of insoluble hydroxides when the solution is neutralized with sodium hydroxide.

As the extraction raffinate is generated, it is pumped to a stainless steel neutralizer tank which holds a 500-gallon batch (see Figure 1). Thirty-six pounds of barium carbonate is added to the solution. Sulfate is added as 15 pounds of aluminum sulfate or 1.35

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gallons of concentrated sulfuric acid. The mixture is agitated for 15 minutes and then heated to 190° F. Sodium hydroxide is added to yield a pH greater than 8. The solution is filtered through a plate-and-frame filter, and the filtrate is returned for a second treatment with barium and sulfate. After retreating and refiltering, the solids are collected in 55-gallon drums for shipment to an approved burial ground. The filtrate is combined with other Pilot Plant liquid wastes and is pumped to a central treatment facility called the General Sump.

In the General Sump, aqueous process effluents from all production plants are collected in large tanks (see Figure 3). The waste is adjusted to a pH greater than 8, and a flocculating agent is added. After mixing, the treated waste is discharged to one end of a 4.5 acre rubber-lined settling basin (Figure 4) which has a capacity of 23,000,000 gallons. The discharge from the opposite end of the basin is mixed with water from the storm sewer system, the sanitary sewage treatment plant, and the combined effluent is discharged to the Great Miami River via an underground pipeline. These major effluent streams are sampled and analyzed daily. If needed, the rate of release from the settling basin is reduced to maintain drinking-water standards in the river.

Table I contains typical analytical data for the Pilot Plant wastes before and after the Pilot Plant treatment. The radium-228 concentration is further reduced by the General Sump treatment, basin settling, and dilution with radium-free streams from other sources, prior to discharge to the river. After dilution in the river, the

concentration of radium-228 is less than 5 disintegrations per minute per liter; the maximum permissible concentration for drinking water is 66 d/m/l.

TREATMENT OF OTHER LIQUID WASTES

Another major waste liquid is the filtrate obtained from the precipitation of thorium tetrafluoride. About 1000 gallons per day are produced. Treatment of this waste depends on the concentration of radium-228, and the amount of this isotope present depends on the length of time since the thorium was last separated from its daughters. If recently refined thorium is used, the filtrate will have a low radium concentration, and neutralization of the free hydrofluoric acid is the only treatment needed. If the thorium feed has been stored for several years, the amount of radium-228 will be significant, and the filtrate will be given the barium sulfate treatment for radium removal.

In general, radium-free wastes are collected, neutralized with sodium hydroxide, and filtered. If the drummed filter cake contains enough thorium or uranium, it is stored for later recovery. If reprocessing is not warranted, the cake is dumped in an on-site burial pit.

Despite the containment of specific process wastes, a considerable amount of liquid still reaches the Pilot Plant floor. Collection and treatment of this waste is needed because of the acidity or because the waste contains recoverable amounts of uranium or thorium. Recently, improvements were made in the system for drainage collection and

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treatment. These improvements were needed to prevent ground contamination, to reduce chemical damage, and to provide a system which would separate drainage from uranium and thorium operations.

Until the recent waste handling changes, floor drainage from Pilot Plant thorium and uranium operations was collected in two below-grade sump pits (8 feet by 8 feet by 12 feet deep) located outside the plant. The liquid flowed to the pits through floor drains and buried pipes. The north pit received all the floor drainage and outside pad drainage. This liquid was pumped back to tanks inside the plant for treatment. Whenever simultaneous thorium and uranium operations were carried out, the floor drainage would contain both of these valuable materials. Uranium can be recovered from wastes contaminated with thorium. However, thorium cannot be economically recovered if the uranium content is high.

The south pit collected filtrate from neutralized waste, steam condensate, and water from an outside interceptor sump, which is the collection point for an underground drainage tile system. Liquid collected in this sump was relatively clean and did not require local treatment. It was automatically pumped to the General Sump where it was mixed with other liquid wastes, treated, and discharged to the Great Miami River or the settling basin.

When originally installed in 1951, the two outside sump pits had stainless steel linings. These linings soon bulged inward and cross-stays were added to keep the linings in place. During 1960-1961, the stainless steel linings became badly corroded by waste liquors containing large amounts of hydrochloric, hydrofluoric, and sulfuric acids.

The remaining stainless steel lining was then removed, the concrete patched, and a new lining of nonalloy steel was installed. A special plastic lining (having the trade name, Fligid) was applied to the steel liner. This material consisted of a flexible, relatively soft layer of plasticized polyvinyl chloride next to the steel and an outer layer of rigid unplasticized polyvinyl chloride which has better resistance to corrosive chemicals and high temperatures than the plasticized PVC.

This lining remained intact for several years until solvent extraction operations were resumed in the Pilot Plant in 1965. Continued exposure to solvents with an organic-phosphate base and aromatic hydrocarbon diluent destroyed the composite PVC liner. The underlying steel liner and concrete wall were also heavily damaged in places, especially near the point where the plant floor drainage entered the sump pit. The buried floor drains in the plant were also known to be leaking, allowing liquid to collect under the plant floor in cavities caused by corrosive action of the waste.

Because of the damage and the need to prevent mixing of thorium and uranium wastes, the collection and treatment system was altered in early 1970. A system of floor trenches was installed to replace the floor drains and buried pipe. Floor liquids now drain to the trenches and flow to four small below-grade sump pits (see Figure 5). The trenches and sumps are located so that the trenches can be blocked, as required, to permit the separate and simultaneous collection of wastes from the thorium and uranium processing areas. From the small sump pits, the liquid is pumped to either of two 8,000 gallon above-

ground stainless steel accumulator tanks (10 feet in diameter and 14 feet high). One tank is used for thorium wastes and the other for uranium wastes. Wastes are pumped from the accumulator tanks to either of two neutralizer tanks where an alkali is added to neutralize the acid and precipitate the uranium or thorium. Each neutralizer tank has a plate-and-frame filter to collect the solids. The neutralized filtrate is eventually pumped to the General Sump for final disposal. The filter cake is drummed and stored if it contains enough thorium or uranium to justify reprocessing. If recovery is not justified, the cake is dumped in an on-site burial pit. The two outside sumps have been repaired and relined. They now receive only clear water or neutralized waste.

Approximately 325 feet of trench was installed. The trench is 6 inches wide and the depth varies from 6 to 15 inches. The depth variation is due to changes in the floor level. The trench bottom is level throughout the system to permit trench blocking and draining as needed to prevent mixing of thorium and uranium wastes. To prevent chemical damage to the concrete, the trench is coated with a resistant polymeric material called Ceilcote 6400B. The trenches and sumps are covered with a stainless steel grating. Stainless steel piping is used for the transfer of untreated liquids. Carbon steel piping is used for the transfer of neutralized wastes.

CONTAMINATED DRY SOLIDS

Only small amounts of contaminated dry solids are produced in the Pilot Plant. Combustible solids are sent to the plant incinerator.

Noncombustible solids are sent to an on-site burial pit. Waste oil and solvent are burned in a special burner and the ash is drummed for later reprocessing (see Figures 6 and 7).

The slag which is produced when thorium fluoride is reduced to thorium metal is buried at the on-site disposal pit. Although the slag contains thorium, the concentration is not high enough to warrant recovery.

Contaminated graphite from the Pilot Plant's uranium operations is processed for material recovery. Graphite crucibles are used for the melting and casting of uranium under vacuum. Impurities, including the daughter products of uranium, migrate to the top and to the side of the molten metal. The impurities and small amounts of uranium also penetrate the graphite. After several uses, a graphite crucible contains enough uranium to make recovery economical.

Crucibles are used until they fail; then they are stored for several months to allow uranium daughter products to decay. These daughters, thorium-234 and protactinium-234, decay with a half-life of 24 days. After the holdup, the graphite is broken and burned in a simple outdoor burner (see Figures 6 and 8). The ash, which contains 10-30% uranium, is returned for reprocessing.

AIRBORNE WASTES

To prevent worker exposures to dusts and vapors, dusty operations are carried out in ventilated equipment or enclosures. Bag-type dust collectors remove airborne particles before the exhaust is discharged

to the atmosphere. This material is drummed for later reprocessing. Since the exhausts from the oven drying and retort calcining of ThF_4 contain acid, these air streams are passed through scrubbers containing a caustic solution. The spent scrubber solutions do not contain recoverable amounts of material; hence, they are combined with other liquid wastes for disposal as previously described.

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2. W. Burkhardt, G. G. Briggs, A. L. Clavel, J. F. White, Production of Dense Thoria, USAEC Report NLCO-1029, July, 1969.

TABLE I

EFFECT OF WASTE TREATMENT ON EXTRACTION RAFFINATE, TYPICAL VALUES

	RAW	TREATED
Radium-228 beta radioactivity, d/m/l(1)	10^7	10^4
Total Beta radioactivity, d/m/l	10^7	10^6
Total Alpha radioactivity, d/m/l	10^7	10^6
Thorium, mg/l	~1	-
Fluoride, mg/l	~1	-
HNO_3, M	0.5-2	-
pH	<1	11

(1) d/m/l = disintegrations/minute/liter.

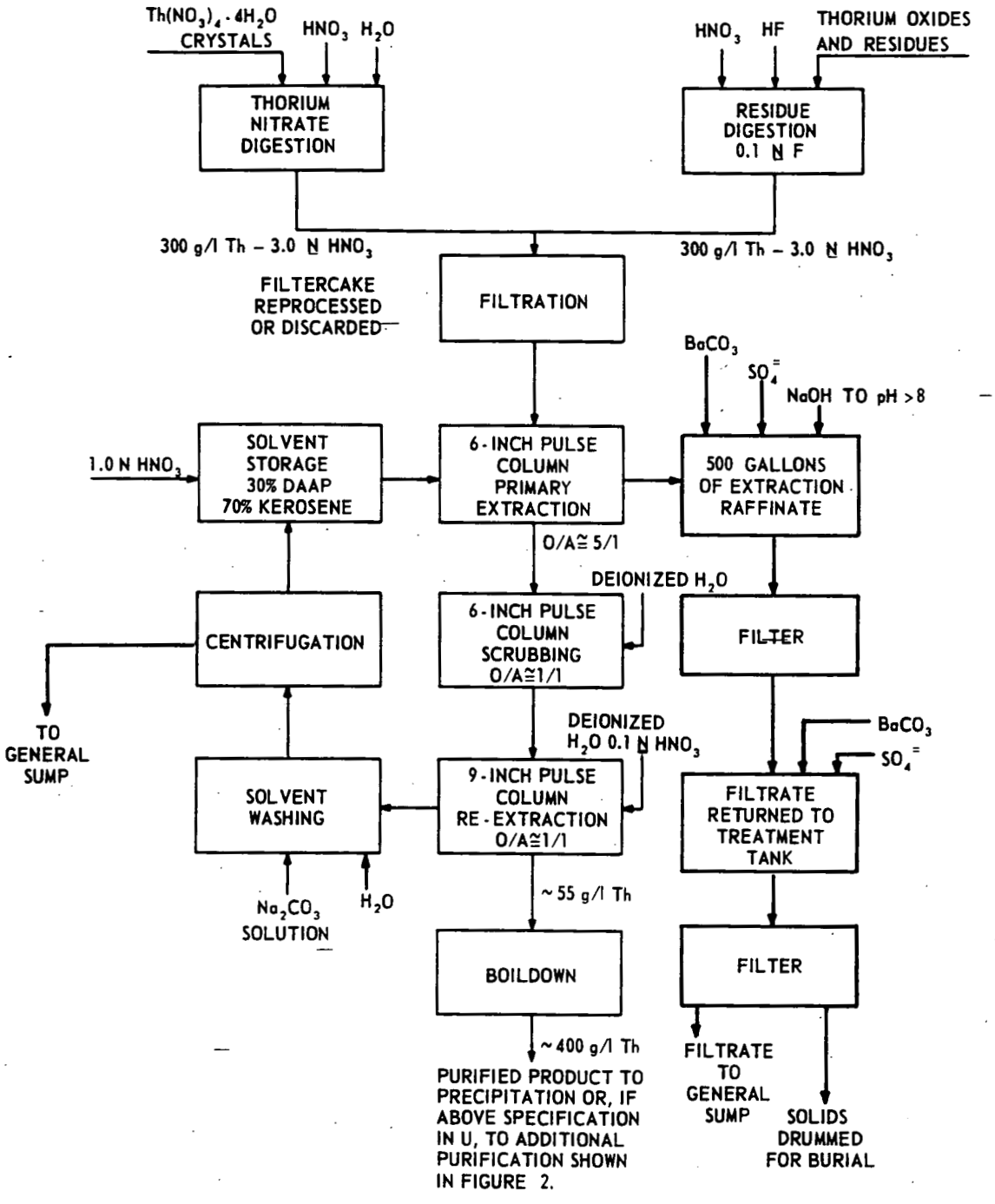

FIGURE 1 Thorium Purification Cycle Using Diamyl-Amyl Phosphonate

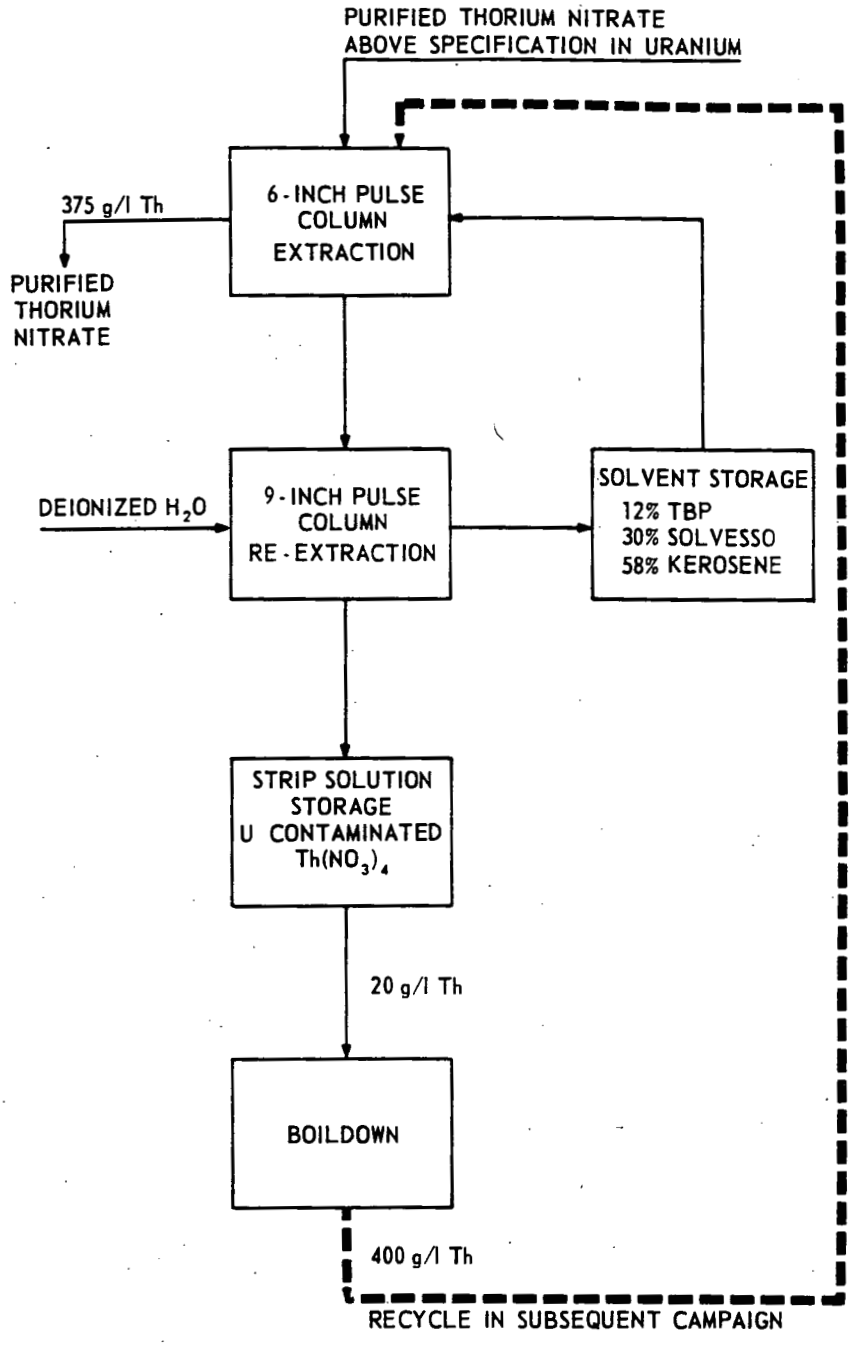

FIGURE 2 Flowsheet for Removal of Uranium from Thorium Nitrate

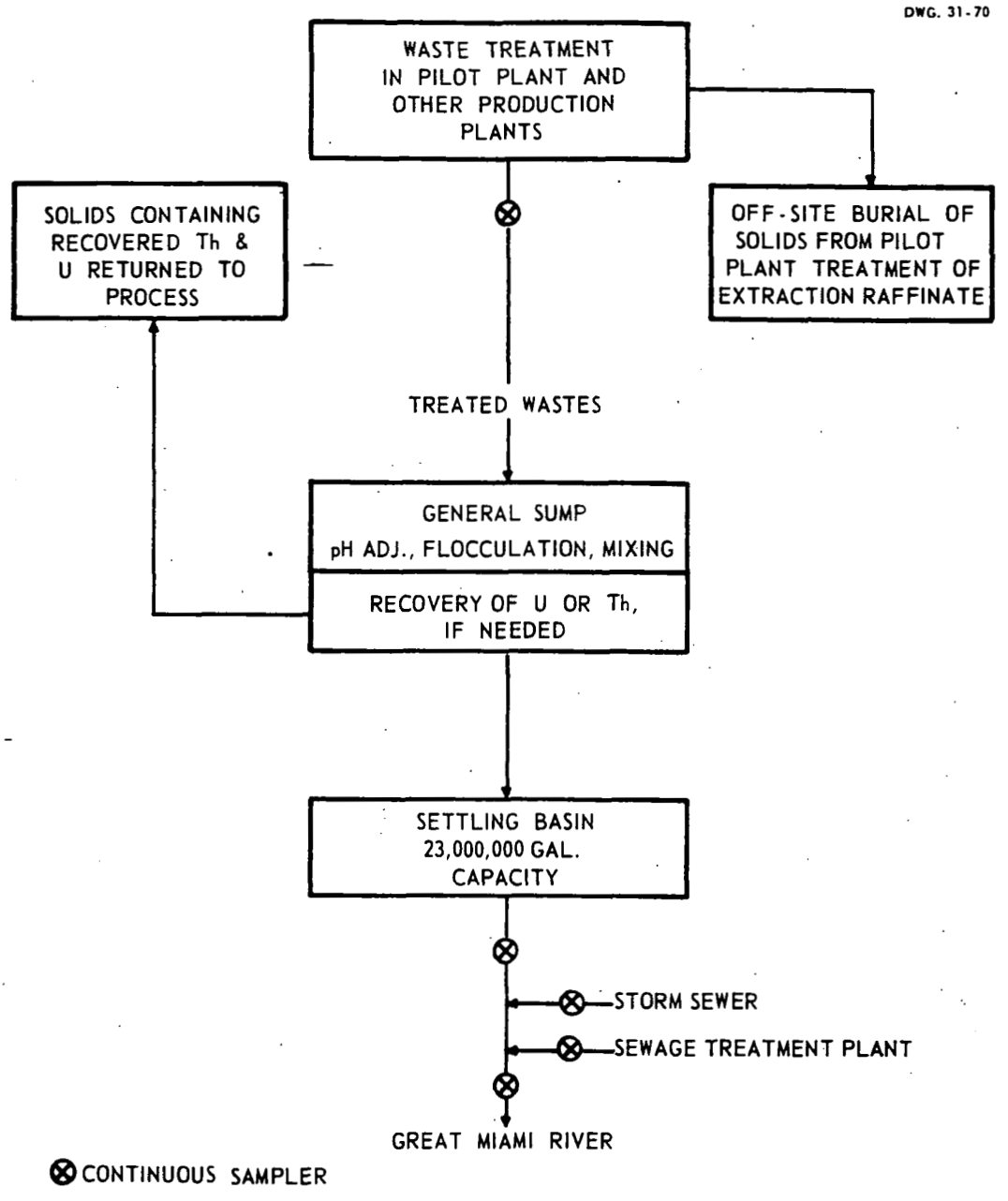

FIGURE 3 Plant-Wide Waste Treatment Process

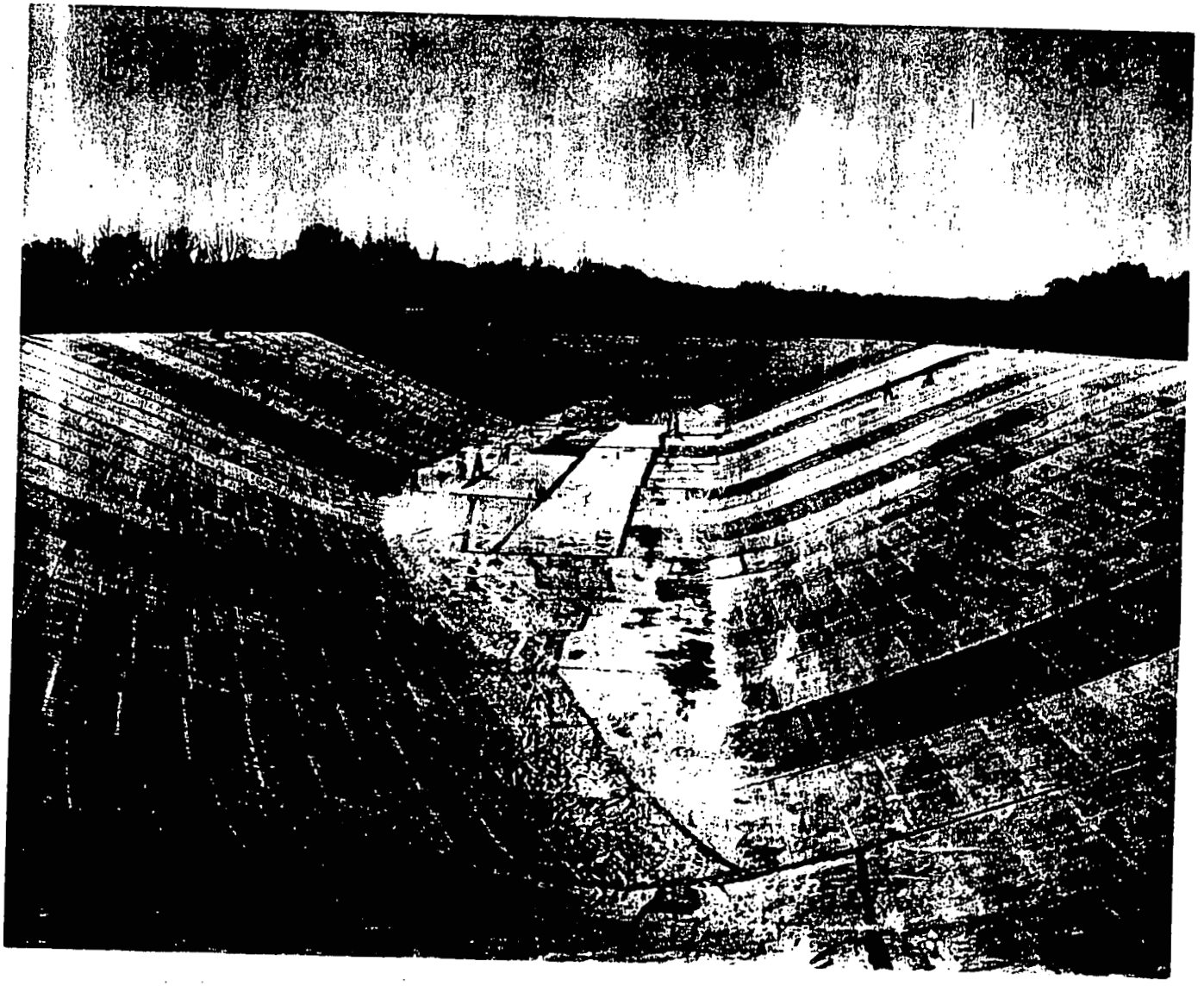

FIGURE 4 Rubber Lining Being Installed in Settling Basin

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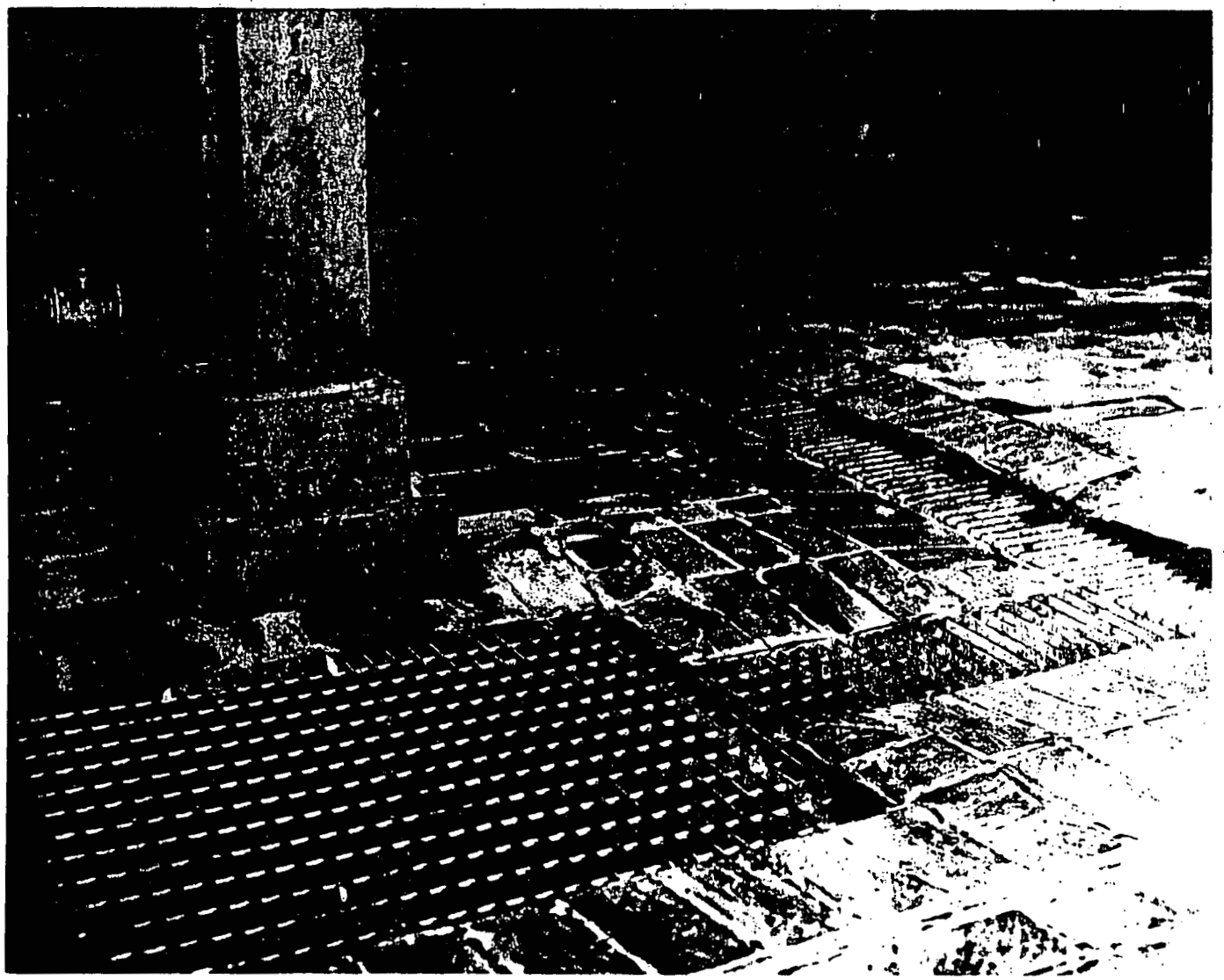

FIGURE 5 Floor Trench and Sump

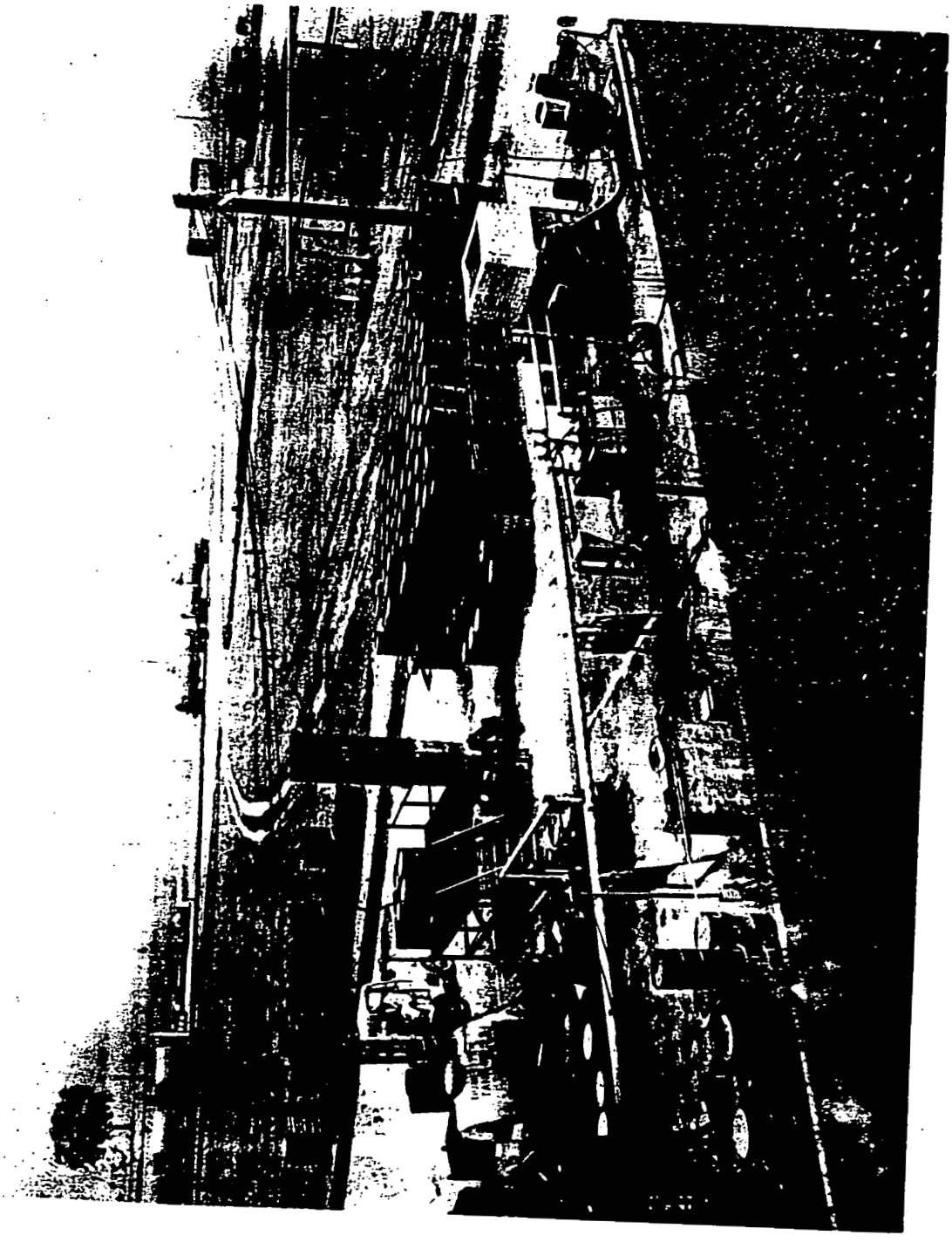

FIGURE 6 Pad Area Showing Graphite Burner and Oil Burner

FIGURE 7 Close-Up of Oil Burner in Operation. Note Absence of Visible Stack Emissions.

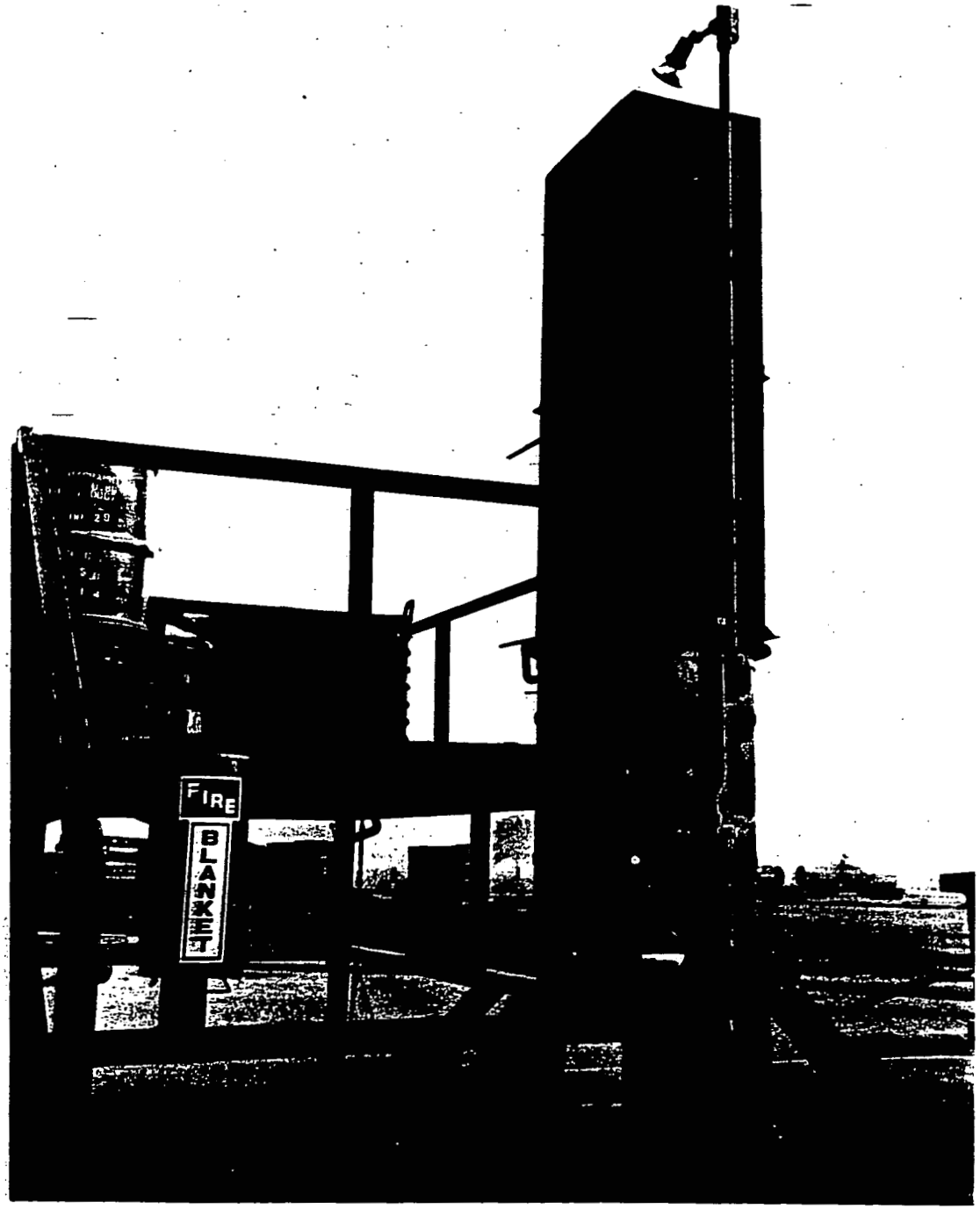

FIGURE 8 Graphite Burner in Operation