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RADIOACTIVE WASTE MANAGEMENT

VOLUME TWO

R. E. Blanco and Wallace de Laguna

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TREATMENT OF LOW LEVEL WASTES BY CHEMICAL METHODS[*]

R. E. Blanco

Chemical treatment of liquid radioactive wastes is carried out to a considerable extent at most atomic energy establishments throughout the world. In general the decontamination factors achieved are not very high but the method is economical and practicable for the large volumes of relatively low-level activity waste which arise daily. When higher decontamination is desirable, this method is often used as a first stage to be followed by further treatment using ion-exchange and/or evaporation techniques.

The main object of chemical treatment is to concentrate the radionuclides present into a small bulk of insoluble sludge which can then be separated. This reduces the activity level of the effluent which can be either disposed of to the environment or retained for a second stage treatment.

SLIDE 1 Advantages of Chemical Treatment (69-8609)

The choise of precipitation method to be used depends on many factors: — the radionuclides present, the decontamination factor required, and the inactive constituents in the effluent. In general, the aim is to render the radionuclides insoluble so that they can be easily separated from the treated liquid. Owing to the very small weight of radioactive material likely to be present, it is not sufficient merely to form insoluble compounds of the radioisotopes, it is also necessary to precipitate and coagulate the finely divided particles so that they can be removed. To achieve this, coagulants are used which will co-precipitate some of the radionuclides with the inactive ions present and also absorb some of them direct from solution. In addition, since most effluents contain some suspended solids on which radioactive matter is absorbed, this too must be removed so it is necessary to use chemicals which will produce absorbent and heavy flocs. The hydroxides, carbonates, and phosphates are very effective because of the low solubilities of the precipitates formed with fission products.

Segregation of wastes is desirable to lower costs and to prevent materials from entering the treatment system which would interfere with the treatment.

The person producing waste prefers to have a single waste system into which he places all his waste. At nuclear establishments this results in a large volume of slightly contaminated waste to be treated. Conversely, the waste processor prefers wastes to be segregated at origin into many classifications by physical state and concentration. This results in the treatment of smaller volumes of waste at a somewhat higher activity level but with a large part of the waste able to be released to the environment either without treatment or with minimum treatment. Either of the above philosophies, if taken to extremes, wastes effort and is uneconomic, and the solution lies somewhere in between.

Even when segregation is extensively practiced and all liquid wastes with higher than the upper level set for the low-level activity category are placed into containers especially provided for the purpose, it is advisable to further segregate the low-level liquid wastes into several different categories as shown in the next slide.

(*) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation. Notes for lectures on Nuclear Waste Treatment and Fuel Reprocessing presented at the Institute de Energia Atomica, Nuclear Engineering Division, Cidade Universitaria, São Paulo, Brazil, October-November, 1969.

SLIDE 2 Segragation of Liquids (69-8605)

SLIDE 3 Materials which Interfere with Collection or Chemical Treatment (69-8602)

a) The amounts of detergents used should be limited. Extra amounts of precipitants are required which increases volume of solid waste.

b) EDTA and polyphosphates are used extensively for decontamination. If common sense is practiced with the use of the above materials, it will usually be found that very little trouble to the waste-treatment system will be caused by their use for normal purposes.

COAGULATION AND FLOCCULATION

There are three steps in the process of coagulation and flocculation.

First, the coagulating chemicals are added to the liquid. To ensure that the chemicals are distributed evenly and promptly throughout the liquid, **rapid agitation or mixing** must accur. It is extremely important that rapid or flash mixing of the coagulant chemical occurs, otherwise the coagulant would slowly disperse and the initial chemical reactions would be limited to that point at which the coagulant was introduced. This may produce reactions other than those intended.

Secondly, coagulation, i.e., complex chemical and physicochemical reactions and changes, occurs, leading to the formation of finely divided precipitating solids.

Lastly, by means of **gentle agitation** of the liquid, flocculation takes place, i.e., the finely divided particles contact and adhere to one another and form progressively larger floc. This insoluble flocculent precipitate will then settle out, carrying with it the coloidal materials present in the liquid. It may be assumed that the floc traps the colloidal matter in three main ways:

a) By simple mechanical entanglement with the floc;

b) By adsorption of the colloid on the floc; and

c) By neutralization of the positively charged colloidal particles by the negatively charged colloidal floc first produced.

SLIDE 4 Important Precipitation Conditions (69-8603)

a) The optimum precipitation conditions are often very narrow and must be determined in both small-(jar) and large-scale tests.

LIME-SODA PROCESS

SLIDE 5 Reactions in the Lime-Soda Process (69-8604)

a) A standard method for the removal of water hardness on an industrial scale consists of the addition of lime and soda-ash to precipitate carbonates and basic carbonates of all cations except the alkali metals.

Where only temporary hardness (i,e., bicarbonate) is present, sufficient lime is added to precipitate carbonates including calcium carbonate, but if permanent hardness (i,e., sulphate) is present, excess soda-ash must be added as well to ensure complete removal of the magnesium and calcium as carbonates; the doses of lime and soda-ash are calculated from analyses for temporary and permanent hardness.

In permanently hard waters soda-ash is first added equivalent to the permanent hardness, followed by lime to give the pH necessary for optimum treatment. At high concentrations of magnesium ($>$ 60 ppm) excess lime is required to precipitate magnesium hydroxides at a pH greater than 10.5 and the final effluent then has a higher total solids content than that from waters containing little magnesium. The chemical equations are as shown in this slide.

b) Strontium is also removed by this treatment; the degree of removal is greater than that predicted on the grounds of its solubility product alone, which suggests the formation of mixed crystals of calcium carbonate and strontium carbonate. The removal of strontium parallels hardness removal and is more effective in the hot process, e.g., at 96°C its increased removals are obtained if an excess of soda-ash is used above that equivalent to the permanent hardness.

c) Since 1960 the plant at Marcoule has been treating its low-activity effluents ($<$ 1 μCi/ml) with the soda-lime process instead of the calcium-phosphate process used before. The over-all DF is slightly higher (12 vs 10) and the DF for strontium has increased to an average of 100. A modified process involving inactive strontium carbonate precipitation after soda-lime treatment has been tested on an industrial scale. The final amount of sludge is three to six times less than that obtained with the soda-lime method.

SLIDE 6 Lime-Soda Treatment of Low-Level Waste at ORNL (69-8600)

a) Cesium removal is low with the lime-soda method so a clay(illite) is added to sorb the Cs.

b) Requires a pH of 11 and a residual calcium content of $<$ 15 ppm.

SLIDE 7 Reactions in the Hydroxide and Phosphate Precipitation Process (69-8601)

a) A conventional method of water treatment consists in adding aluminum or ferric salts and then raising the pH by addition of lime, soda-ash or caustic soda to precipitate the hydroxides of these metals. These methods have been applied to decontamination of low-activity liquid wastes. The reagents used include alum, sodium aluminate, ferric salts or crude chlorinated copperas (ferrous sulphate oxidized by treatment with chlorine).

b) Hydroxides and basic carbonates of many polyvalent cations are co-precipitated and these tend to be absorbed by the flocculant precipitate; only the alkaline metals and to some extent the alkaline earths are unaffected. In addition to acting as a weighing medium in solutions of low solids content where otherwise the total quantity of precipitate might be too small to settle the bulky aluminum or ferric hydroxide precipitate also clarifies the final effluent by filtration if the system is so designed that the treated effluent is drawn off through a blanket of the floc. When formed under alkaline conditions the floc is negatively charged owing to adsorption of hydroxyl ions and will therefore adsorb positive ions but not negative ones such as iodide ion. Positively charged suspended matter is also efficiently removed, the suspended particles acting as nuclei for growth of the floc particles.

c) The efficiency of removal is improved by the presence of sulphate ions at turbidities greater than 5 ppm. Sodium aluminate is not used alone but with alum to obtain some special results, e.g., the failure of some very cold waters to coagulate with alum alone may be overcome by adding about 3.4 ppm sodium aluminate with the alum.

d) Generally with alum, soft waters of low mineral content coagulate best over a narrow range of pH values between 5.8 to 6.4, whereas harder waters coagulate quite readily at pH values of 6.8 to 7.8. Ferric hydroxide coagulation can be used at higher pH values.

e) Ferric hydroxide flocs usually give better removals than aluminum hydroxide ones because of the higher pH at which the former can be precipitated; soda-ash gives somewhat better results than sodium hydroxide because of a slight removal of strontium and increased removal of other elements as basic carbonates. Phosphate removals are better in hard waters than in soft ones because of precipitation of Ca_3PO_4. The addition of clays such as kaolinite or bentonite to soft waters often improves maximum removal.

f) At Windscale, United Kingdom, the coagulation method used is to raise the pH of the liquid with soda-ash to 8 after the addition of alum (20 ppm Al). A similar process is used at Lucas Heights, Australia, where the coagulation is generally carried out at a slightly lower pH and with a lower concentration of alum, depending on the results shown by jar tests. With a suitable design of equipment, the DF obtained is about 10.

SLIDE 8 Ferric Hydroxide Treatment of Low Level Waste at the Moscow Station After Coagulation and Filtration (69-9222)

a) In the USSR as part of a complex treatment process, coagulation is carried out with ferric sulphate (100 ppm Fe) and by raising the pH to 10 with caustic soda. The ferric salt is found to be particularly useful for effluents containing soap and suspended matter and gives good removals of approximately 90% for the rare earths, zirconium and niobium, but poorer results for ruthenium and strontium and virtually no removal of cesium. When iron salts are used, it is considered that the multivalent cations, yttrium, cerium, promethium, and ruthenium are absorbed throughout the volume of the sludge while strontium and calcium are taken up on the surface only. In consequence, the alkaline earths tend to be released to a much greater extent than are the multivalent elements.

b) When plutonium is the principal contaminant, the addition of iron salts aids decontamination. The ferric hydroxide co-precipitates, adsorbs the plutonium and binds it to a form very resistant to leaching by water. The process together with filtration gives sufficiently low residual plutonium content to allow direct release of the effluent to the environment. A similar process has been studied and applied in batch operation at Livermore. A more complex treatment for plutonium, in two stages, is used at Rocky Flats. In the first step, neutralization and ferric hydroxide lime precipitation occur; in the second stage, ferric hydroxide precipitation is provided by ferrous sulphate oxidation with calcium hypochlorite in the presence of excess lime.

PHOSPHATE PRECIPITATION

Coagulation with phosphate has been very satisfactory at a number of nuclear establishments for treating low-activity liquid waste. Generally trisodium phosphate has been the coagulant, but in some places monosodium phosphate has been used. At Harwell the low-activity liquid waste is treated by raising the pH to 9.5 with caustic soda and then adding excess trisodium phosphate. With more active wastes, the pH is adjusted to 11.5 with caustic soda, then tri-sodium phosphate (and calcium chloride if calcium is below 50 ppm is added so that the ratio $Ca^{2+}/(PO_4{}^{3-})$ is 5/8. To produce a denser floc, ferric sulphate (or ferrous but oxidized at elevated pH) is also added as a conditioning agent to give a concentration of 40 ppm Fe^{3+}. Higher doses for calcium (300 mg/liter) and phosphate [ratio $(PO_4{}^{3-})/Ca^{2+} = 5/1$] have been investigated in the USSR.

It is probable that a hydroxyapatite is formed of probable composition $3Ca_3(PO_4)_2 . Ca(OH)_2$. There is evidence that this compound has considerable cation exchange capacity and further that certain cations, notably strontium and plutonium, are incorporated into the apatite lattice.

The phosphate process can remove more than 99% of α-activity and about 90% of the β-activity from wastes containing mixed fission products. The removal of ruthenium varies according to the ionic form in which it is present and the removal of cesium is generally poor.

TROUBLESOME RADIONUCLIDES

Ruthenium — One of the most troublesome nuclides to remove from liquid wastes is ruthenium, since it can be present in the cationic, anionic, or non-ionic form. Apart from ion-exchange methods, the best removals have been obtained by co-precipitation with copper sulphide in acid solution. Since it is not always possible or desirable to work at low pH values, one treatment employed at Harwell is the formation of a ferrous sulphide precipitate by the addition of ferrous sulphate and sodium sulphide at pH values above 8.0. The optimum dosages are 20 ppm Fe^{2+} and 20 ppm S^{2-}. With certain effluents it is necessary also to add a calcium salt (20 ppm Ca^{2+}) to obtain a satisfactory precipitate. This process normally follows the phosphate treatment and is valuable, since it gives an increase of approximately 5% in the over-all removal of the β-emitters. The efficiency for ruthenium removal is variable, depending on the form present, but the process is particularly useful in removing radiocolloids.

In the Marcoule plant, a treatment used on a pilot-plant scale is particularly efficient for nitrato and nitroso-ruthenium complexes. It mainly consists, after preoxidation in acidic medium, of a co-precipitation of lead paraperiodate. This process provides a DF for ruthenium five times better than the ferrous hydroxide precipitation used before at Marcoule.

Cesium — Cesium is best removed by ion-exchange methods using natural or synthetic zeolites or synthetic organic ion exchangers. An alternative method is the addition of clay during the normal coagulation process as practiced at ORNL.

Some success has been obtained in cesium decontamination by co-precipitation of metal ferro-cyanides. For example: by the addition of 40 ppm of potassium ferrocyanide and 25 ppm of copper as copper sulphate, then, after mixing, adjusting the pH to 8.0 by sodium hydroxide and dosing the mixture with 100 ppm of ferric chloride, one may achieve more than 98% removal. Some other metals are currently used: iron, zinc, cobalt, and, more often, nickel. Above pH 6 and 8, respectively, ferric and copper ferrocyanides lose their effectiveness. For ferrous ferrocyanide (partially efficient for ruthenium removal) the useful pH range is between 4 and 9. Cobalt and nickel ferrocyanides may be used up to pH 10.

Strontium — Strontium is generally removed to a sufficient level by the softening step of effluent treatment. Nevertheless, some investigators have studied precipitation of inactive strontium compounds to give better radio-strontium decontamination.

A strontium phosphate process has been described, which is more efficient at elevated pH. A strontium carbonate process, giving higher strontium removal and up to six times less sludge, has also been studied.

COMBINED PROCESS

SLIDE 9 Combined Ferrocyanide and Lime-Soda Treatment at Saclay (69-8611)

Double and multi-stages for co-precipitations are often operated, combining any of the processes described above. At Saclay and Cadarache, a double treatment comprising, first, cesium removal with nickel ferrocyanides and, second, soda-lime treatment, is generally applied. But the equipment allows the addition of other reagents for special treatments if necessary. Marcoule treats its liquid low-level and intermediate wastes with: paraperiodate for ruthenium, followed by nickel-ferrocyanide and soda-lime softening. In Saclay, DFs are usually of the order of 10 to 60 with a concentration factor of about 60.

SEDIMENTATION EQUIPMENT

The purpose of sedimentation is to ensure the settling by gravity of suspended solids contained in the floc and so to clear the carrying liquid as much as possible. The efficiency of this separation is the controlling element of the whole coagulation-flocculation-sedimentation process, frequently called "chemical treatment". In fact, because the radioactivity concentrates essentially within the sludge to be settled, traces of sludge swept along will have a direct effect on the decontamination obtained in case of direct release or on the efficient duration of runs in case of subsequent filtration.

The theory of sedimentation is complex and of little practical value since floc is not uniform and its basic sedimentation properties cannot be given quantitative value also because the effect of eddy currents in the tank cannot be predicted. However, the main factors that influence sedimentation and which must be evaluated by experience are:

a) Ratio of volume to weight

b) Viscosity and temperature of liquid

c) Period of sedimentation.

SLIDE 10 Typical Batch Equipment (69-8984)

Generally 2 to 4 hr of settling is required.

SLIDE 11 "Accelerator" Sludge-Blanket Clarifier (69-8983)

a) It has been found that in continuous processes the return of about 5 to 15% of the settled sludge to the flash mixer or flocculator improves floc formation and subsequent sedimentation.

b) However, the re-use of sludge has led to the development of a new coagulation-flocculation sedimentation technique commonly referred to as the Suspended-Solids Contact or Sludge-Blanket Clarification process. Water-treatment plant manufacturers in several countries have developed units which are basically similar in that chemical mixing, coagulation, flocculation, sedimentation, and manual or automatic sludge removal are performed in a single tank. In all of them the coagulated water is introduced at or near the bottom of the sedimentation compartment so that upward flow occurs. The water to be treated may enter near the top of the tank, in which case coagulation takes place in a central compartment having downward flow, or it may have chemicals added first and then be introduced directly into the already coagulated water in the bottom. As the rate of the rise of water in the sedimentation compartment is lower than the rate of settling of the heavy floc, the floc remains in suspension to a depth of several feet, through which the rising water passes. This so-called sludge blanket provides contact between the settling floc moving downwards and the smaller residual floc moving upwards with the water. This favors the formation of larger floc through the agglomeration of the fine material. The scavenging action of the previously formed floc leads to the precipitation of insoluble compounds, as well as to the effective removal of fine suspended particles which would not be settled otherwise. The purpose is to secure a floc that will settle at a rate twice that of the upward flow of water, so that separation occurs and the floc does not rise much above a level of 1.5 m (5 ft) below the effluent outlets.

c) The volume of the tank necessary for the complete process is such that a gross detention period of from 1 to 2 hours is provided. This is considerably less than that provided with more conventional units. Often coagulant aids are required for satisfactory operation with the low detention periods that result, especially when the water temperature is low. As these units are small, i.e., have short detention periods, the safety factor is reduced, and careful control is even more essential than with the more conventional units if satisfactory results are to be obtained.

REMOVAL OF SLUDGE

The various types of settlers are fitted with mechanical devices for the removal of sludge. In static settlers the sludges are scraped from the slanted bottom by scrapers with adjustable tilt and depth. These mechanisms attack the sludge layer at a velocity of about 1 cm/s.

Sludges are discharged into a pit from which they are periodically evacuated by pumps, generally of the suction diaphragm type. Preferably, the pumping operation should be performed frequently and during short periods to avoid clogging of the pipes.

For the design of devices intended for removal of sludge, it must be kept in mind that the sludge contains nearly all the radioactivity from the treated wastes, with concentration factors ranging from 25 to 200. Consequently, it is advisable to ensure the biological protection of the personnel by taking the necessary measures on the apparatus as well as around receiving vessels.

The sludge from sedimentation may have three destinations: long-term storage in large underground tanks, subsequent conditioning treatment, or mixing with stabilizing elements for immediate disposal. These different processes are reviewed later.

FILTRATION

Regardless of the type of equipment used to separate flocculent sludges from the treated effluent, this latter still contains small quantities of suspended materials even when clarified. These materials carry co-precipitate radioactive elements and should be removed before the release of the effluent to the environment or to a subsequent processing stage (ion exchange, for exemple).

Two types of filters are used: sand filters (or other granule materials such as anthracite) and precoat pressure or vacuum filters. The function of these filters is not limited to the straining action of passing only particles smaller than the free spaces between granules. Superficial adsorption mechanisms can complete the removal of the finest particles. The filtering precoats do not lead by themselves to a chemical separation but some studies have investigated their replacement by materials having a dual mechanical and chemical action (utilization of ion-exchange filters). For the selective removal of some radionuclides, the importance of the living layer of microorganisms (Schmutzdecke) frequently present on the top layers of sand filters must be emphasized.

SLIDE 12 Typical Rapid Sand Filter (69-8985)

However, as we will see later, many installations achieve satisfactory decontamination without a filtration step.

LABORATORY ASSISTANCE

SLIDE 13 Jar Test Equipment (Photo 96668)

The proper dosages of the chemicals used in chemical treatment can be determined only by trial and error. This determination is made best by submitting a representative sample of the waste to be treated to a series of tests under identical mechanical conditions. The mechanical conditions are maintained constant by utilization of a multiple stirrer. The volume of individual samples should be about one liter. Only one variable should be adjusted per series. That is, maintain the pH at a constant value and vary the coagulant dosage or maintain the coagulant dosage constant and vary the pH. With experience it may be possible to run two sets of three experiments with a six-place stirrer.

SLIDE 14 Imhoff Cone (Photo 96667)

The results of the test, that is, the best dosage, can usually be determined by visual observation. This will include rate of sedimentation and clarity of supernatant. The amount of sludge formed can best be determined by pouring the test sample into an Imhoff cone. However, it may be advisable to perform chemical analyses on the untreated wastes as well as the test samples to determine the degree of removal of the contaminants of concern.

SLIDE 15 Zeta Potential Meter (Photo 97054)

Zeta potential (ZP) is a measurement of electro-kinetic charge (in mv) surrounding each solid particle suspended in an electrolyte solution. This potential is generally electronegative for colloidal materials of raw waters and wastes; it is sufficiently high to allow mutual repulsion between particles to maintain them in suspension.

a) If the electrical charge of colloids is brought back to zero, for example, through addition of colloids carrying positive charges and with moderate stirring (causing numerous collisions without breakdown of formed agglomerates), the repulsing forces are nullified. Particles blend and collect into a flocculus of sufficient size and density to enable sedimentation to occur at an acceptable rate. Zeta potential determination of raw and treated wastes allows the measurement of colloid removal.

b) Consists of microscope, light, micro cell with platinum cathode and anode, and grid screen to measure rate of movement of particles to the electrodes. Rate of movement is evaluated in terms of millivolts (+ or −) of ZP.

c) Zeta potential measurement to improve jar tests, the performance of which were often previously guided solely by visual observation, is frequently used for water treatment. It results in an appreciable improvement in sedimentation and also of subsequent treatments such as filtration and ion exchange. Reagents most in use are alum, activated silica, ferric iron, cationic polyelectrolytes.

Application to the treatment of radioactive wastes has been made at Oak Ridge. For a raw waste with a ZP of − 14 mV, the combined addition of 20 ppm of alum with 0.5 ppm of activated silica leads to the best clarification and a ZP of + 2.5 mV. It was observed that the best procedure consisted in approaching null ZP at ± 5 mV by the addition of alum and adding a little activated silica to complete the dosage. The use of cationic polyelectrolytes (Primafloc C-3) is very efficient at very low doses.

d) Zeta meters are very effective but since they are expensive (~US $3,300), they may not be justified for a small plant.

SLIDE 16 No Title (65-9722)

a) Solids filtered out of treated waste supernatant onto a membrane filter at a Zeta Potential of + 2,5 mV. Jar-test conditions: 30 min of flocculation followed by 30 min of settling.

CHOISE OF PROCESS

If the volume of wastes to be treated is less than 500 or 1000 liters per day, the logical method of choise is batch treatment. The size of the units will depend upon the relative costs of equipment and labor. If labor costs are high, one would want to build a relatively large unit which would be operated only a few days per week; a saving is also effected in the number of necessary analyses. If the labor costs are relatively low, then one would size the plant to be operated once each working day or, in extreme cases, on a 24-hour-per-day basis. It is unlikely that any batch process unit would be smaller than 500 liters.

As a general rule, all nuclear establishments eventually increase in size and complexity and the volume of waste to be treated increases proportionally. It is important, therefore, to plan for increased volume of wastes to be treated in future years. Thus, if one plans to treat only two days a week, the same plant will be adequate for 2-1/2 times the volume if one treats five days a week. Or if it is planned to treat the wastes in one daily shift, the capacity can be tripled by going to a 24-hour-per-day operation.

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1. *Chemical Treatment of Radioactive Wastes*, Technical Report Series Nº 89, IAEA, July 1968.

2. J. H. Clarke, "Chemical Treatment of Liquid Wastes," IAEA Advanced Training Seminar in Radioactive Waste Management, Oxford, September 1967.

3. C. W. Christenson, "Chemical Treatment of Liquids," Basic Training Course in Management of Radioactive Wastes, IAEA-Brazil CNEN, Rio de Janeiro, October 14-25, 1968.

ADVANTAGES OF CHEMICAL TREATMENT

1. Low cost
2. Provides adequate decontamination in most cases
3. Reasonably independent of inactive salts; effective on many waste types
4. Does not retain inactive salts
5. Uses common industrial equipment
6. Relatively easy to operate
7. Removes both ionic and colloidal radionuclides

SEGREGATION OF LIQUIDS

---

a. Liquid from laboratories and working are
which probably contains activity

b. Liquids which probably do not contain
activity (simple treatment to remove
greases, etc.)

c. Sewage - conventional treatment

Products of b and c used to dilute product of a

MATERIALS WHICH INTERFERE WITH COLL
OR CHEMICAL TREATMENT

a. Solid wastes (paper, glassware, etc.)

b. Oil, grease, solvents

c. Highly acid solutions

d. Detergents

e. Complexing agents

IMPORTANT PRECIPITATION CONDITIONS

1. pH
2. Ionic Strength
3. Degree of Mixing and Flocculation
4. Temperature
5. Presence of Suspended Matter (nuclei)
6. Zeta Potential

REACTIONS IN THE LIME-SODA PROCESS

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O \qquad (1)$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 = 2CaCO_3\downarrow + Mg(OH)_2 + 2H_2O \qquad (2)$$

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2\downarrow + CaSO_4 \qquad (3)$$

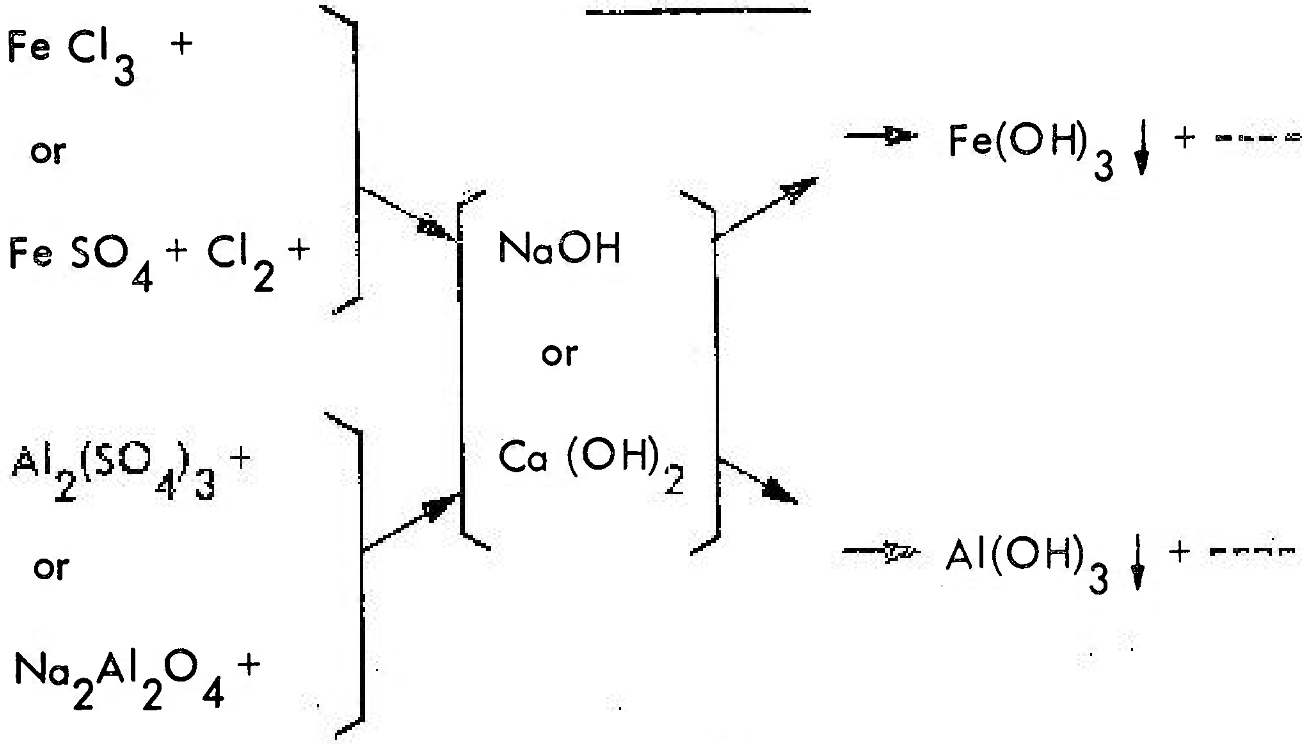
$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow + Na_2SO_4 \qquad (4)$$

LIME-SODA TREATMENT OF LOW-LEVEL WASTE AT ORNL

Period	Average Percentage Removal					
	$^{89+90}Sr$	^{137}Cs	^{106}Ru	^{60}Co	TRE	Gross Beta
Sept. 1957-Feb. 1957	77	--	--	--	79	--
Mar. 1958-Aug. 1959	84	--	--	--	86	--
Sept. 1957-Sept. 1958	--	21	49	65	--	66
Oct. 1958-Aug. 1959	--	86	76	78	--	88
Jan. 1960-June 1961	72	81	72	42	81	--
July 1961-Dec. 1964	74	75	75	73	71	--
Jan. 1965-Aug. 1965	86	81	--	67	--	88

REACTIONS IN THE HYDROXIDE AND PHOSPHATE PRECIPITATION

PROCESSES



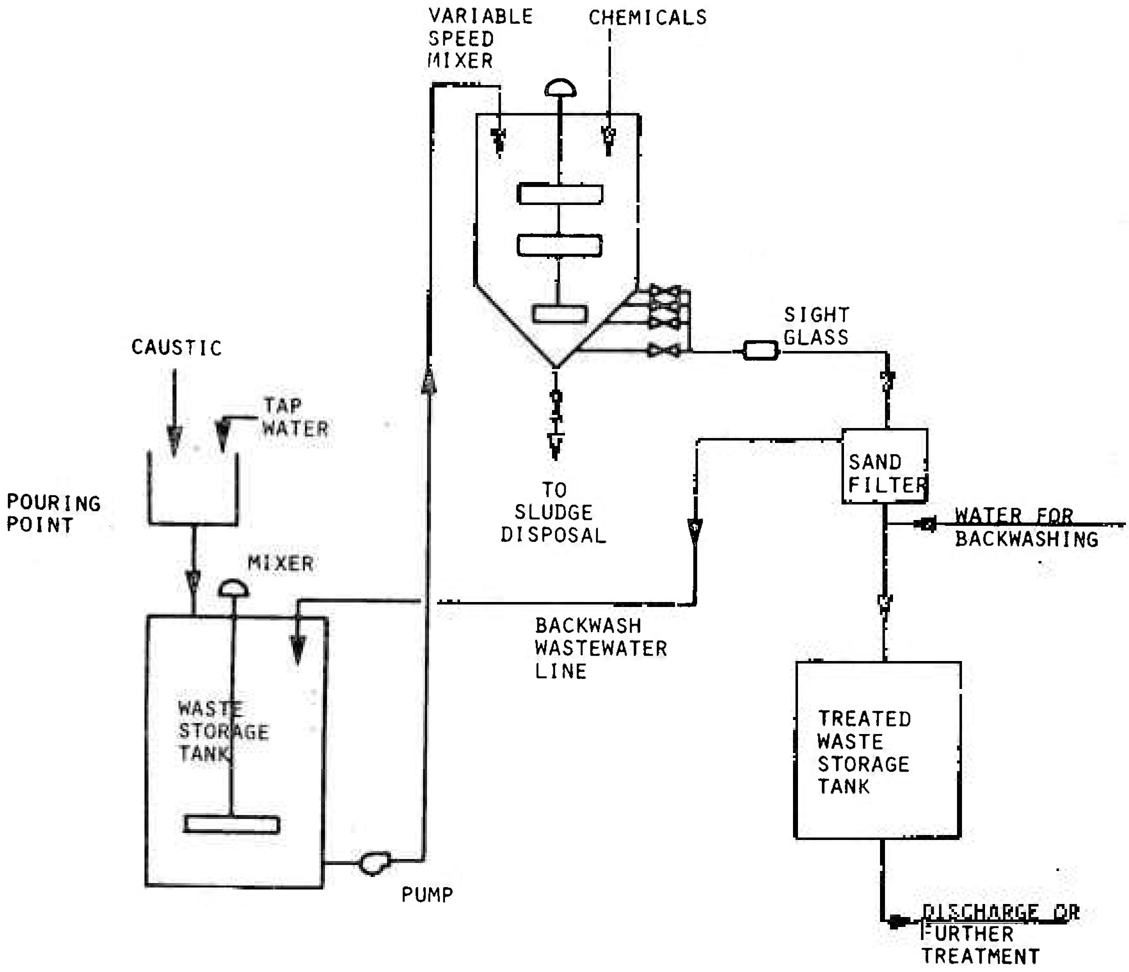
$$3\,CaSO_4 + 2\,Na_3PO_4 \rightarrow Ca_3(PO_4) \downarrow + 3\,Na_2SO_4$$

FERRIC HYDROXIDE TREATMENT OF WASTE AT THE MOSCOW STATION

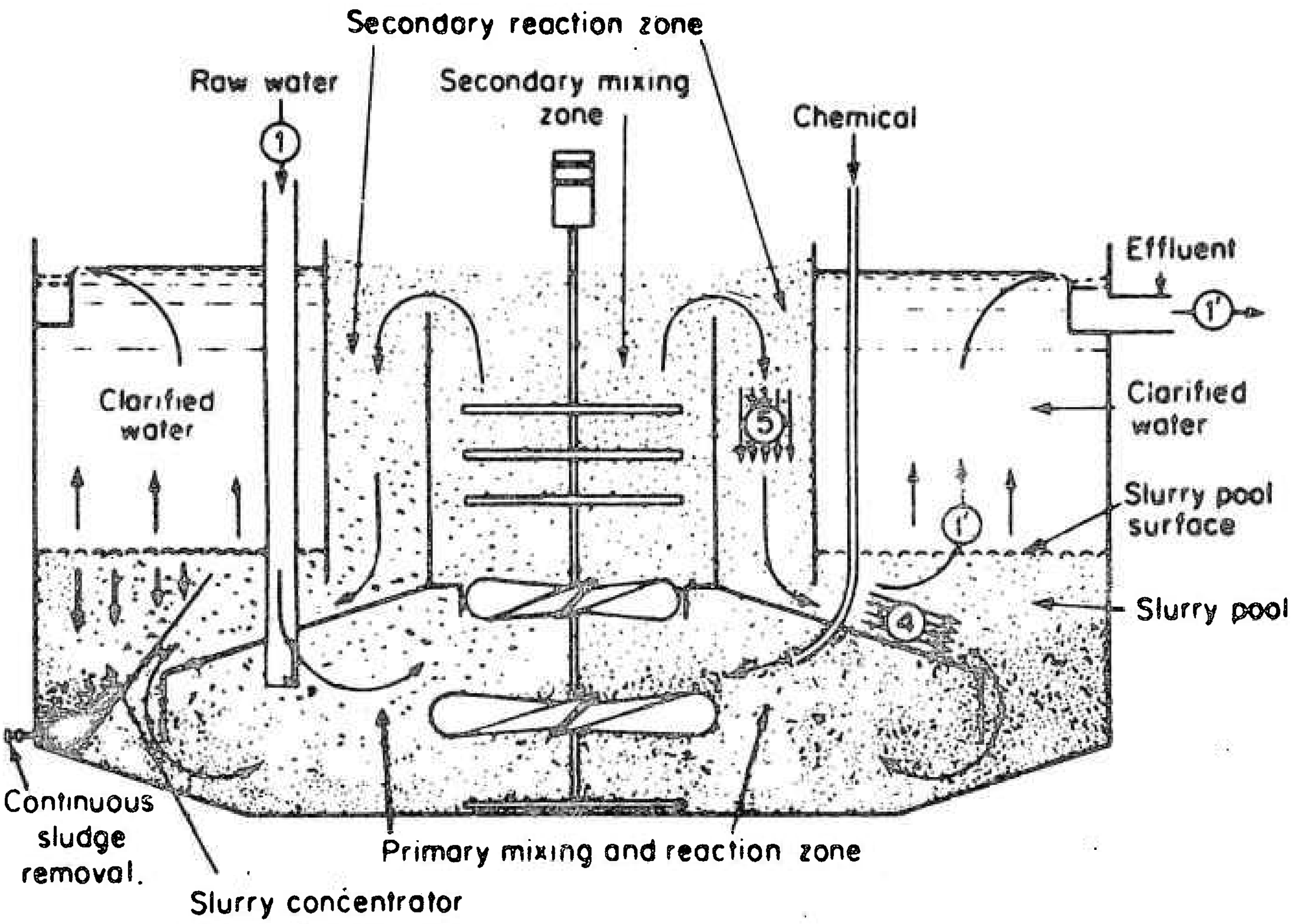
Beta Activity		Before	After	DF	Before	After	DF
Gross	Ci/m^3 x 10^3	2	1.8	1.1	6	5.2	1.15
^{90}Sr	" x 10^5	5	4.1	1.2	1	0.8	1.2
^{90}y	" x 10^5	1.4	0.42	3.3	0.7	0.07	10
^{137}Cs	" x 10^5	2.8	2.6	1.08	2.1	2.0	1.05
^{144}Ce	" x 10^5	20	2.3	8.7	18	0.9	20
^{95}Zr+Nb	" x 10^5	13	0.12	108	1	0.03	75
^{106}Ru	" x 10^5	2.5	0.27	9.2	2	0.25	8
^{131}I	" x 10^5	11	9	1.2	1.5	1.3	1.15
^{35}S	" x 10^3	0.6	0.55	1.1	5.6	5.2	1.08
^{14}C	" x 10^3	1.2	1.1	1.09	0.1	0.08	1.25

COMBINED FERROCYANIDE AND LIME-SODA TREATMENT AT SACLAY

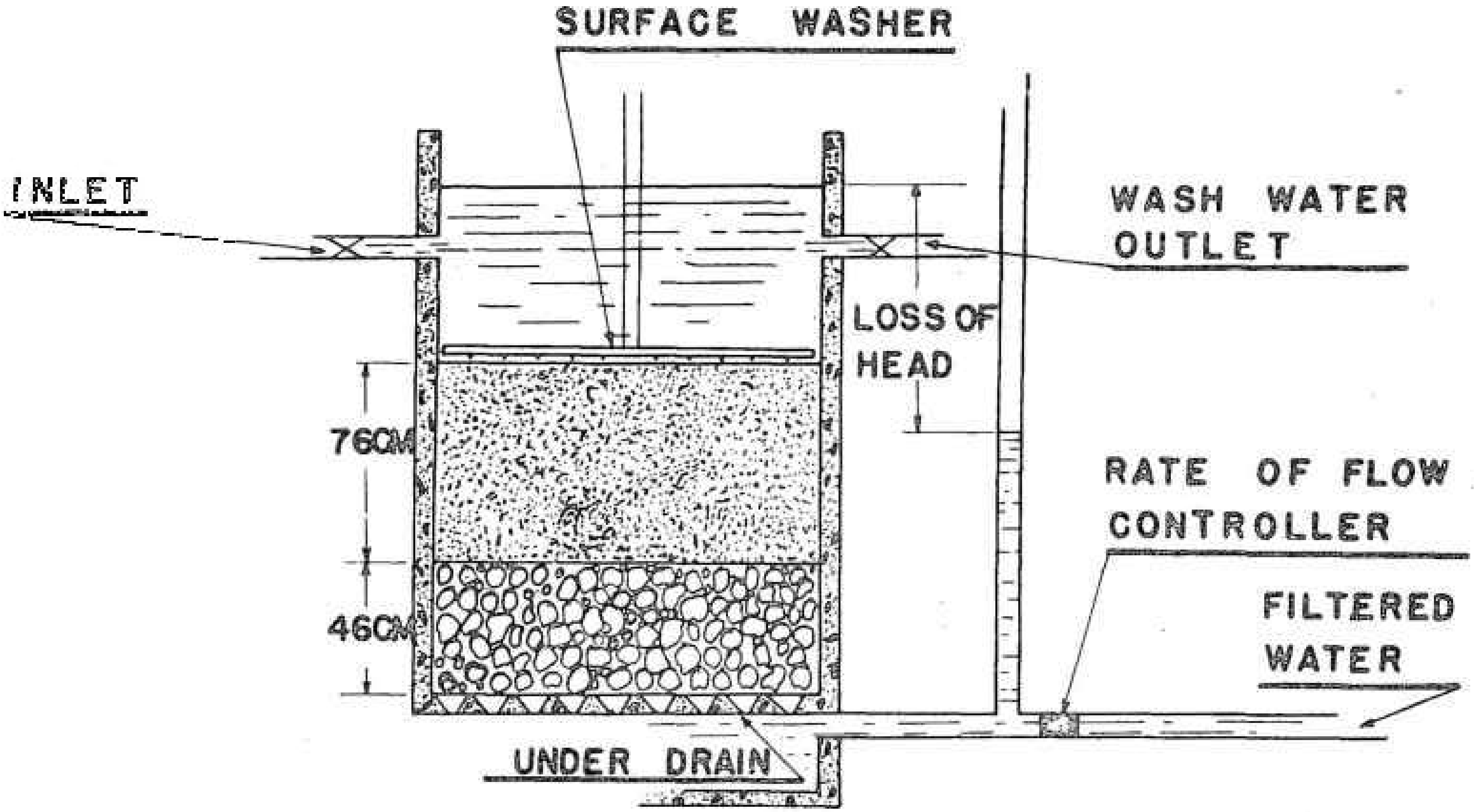
Waste Composition		Decontamination Factors		
Ca^{+2} eq. g/l	Gross β $Ci/m^3 \times 10^3$	Gross α $Ci/m^3 \times 10^3$	Gross β	Gross α
36	9.8	3.3	33	235
30	6.4	5.6	12	850
15	32.	2.8	61	1000
40	9.0	0.33	11	>330
50	1.3	2.0	30	770



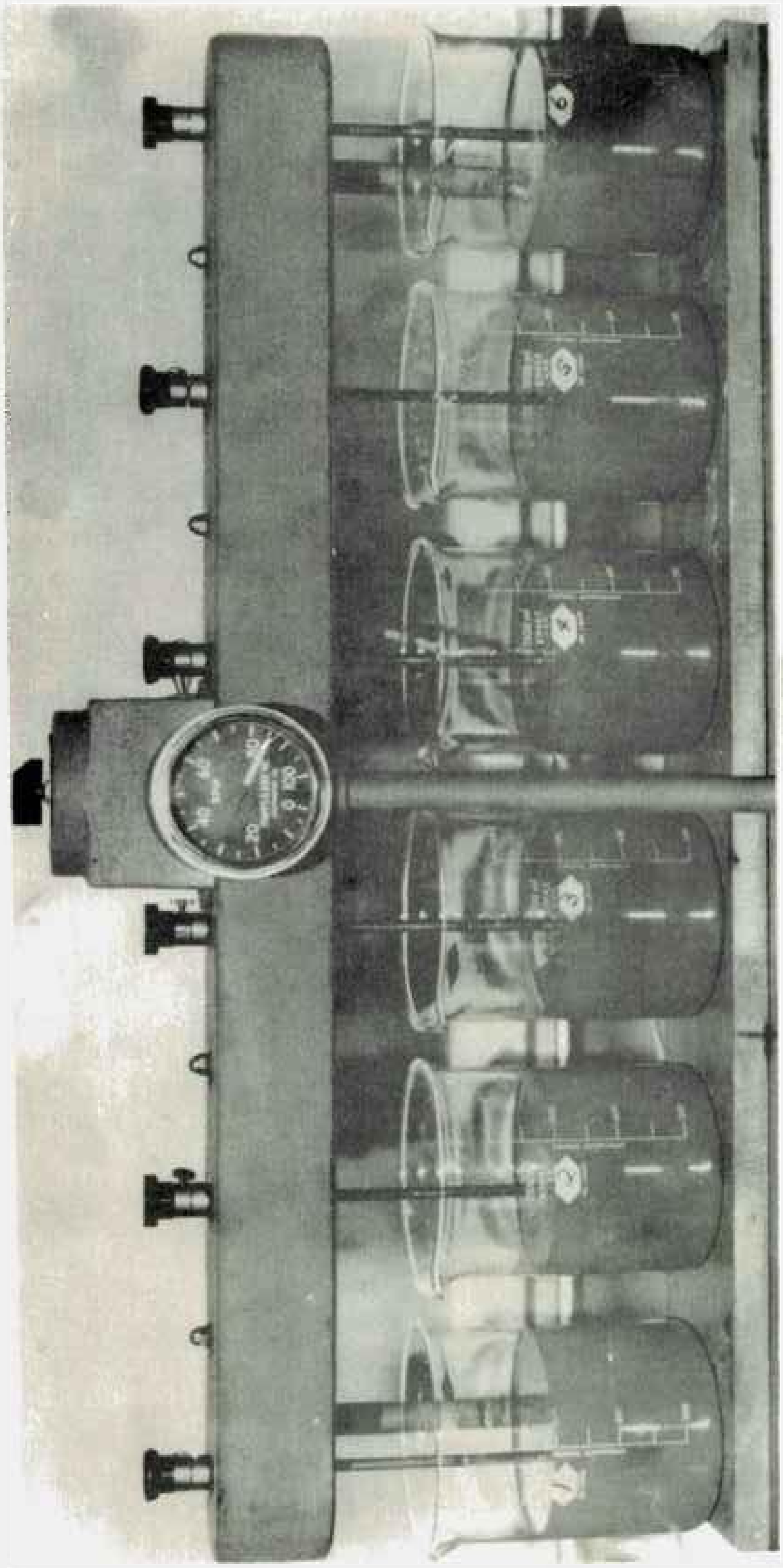
TYPICAL BATCH TREATMENT PLANT



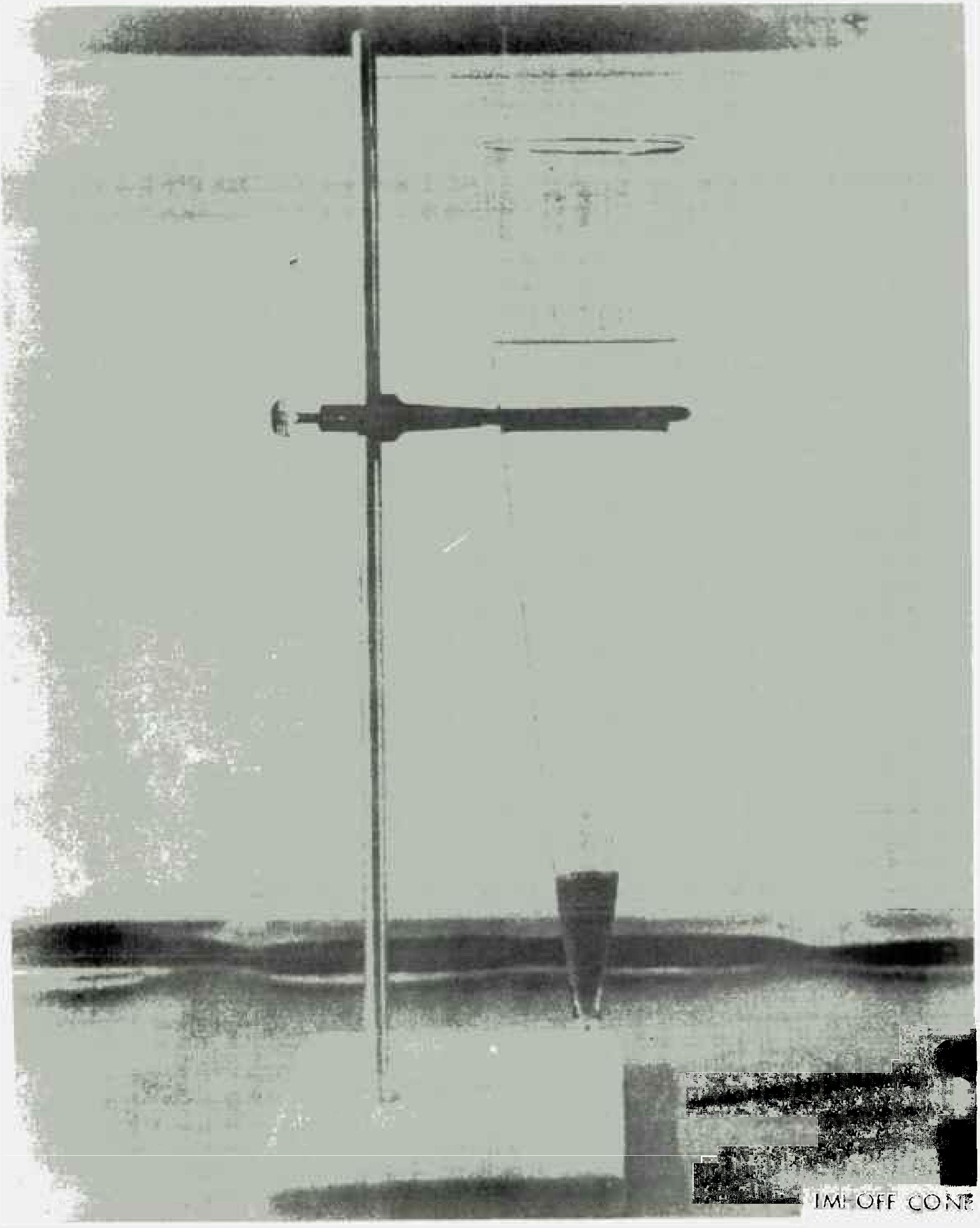
"ACCELERATOR" SLUDGE-BLANKET CLARIFIER



TYPICAL RAPID SAND FILTER



JAR TEST EQUIPMENT



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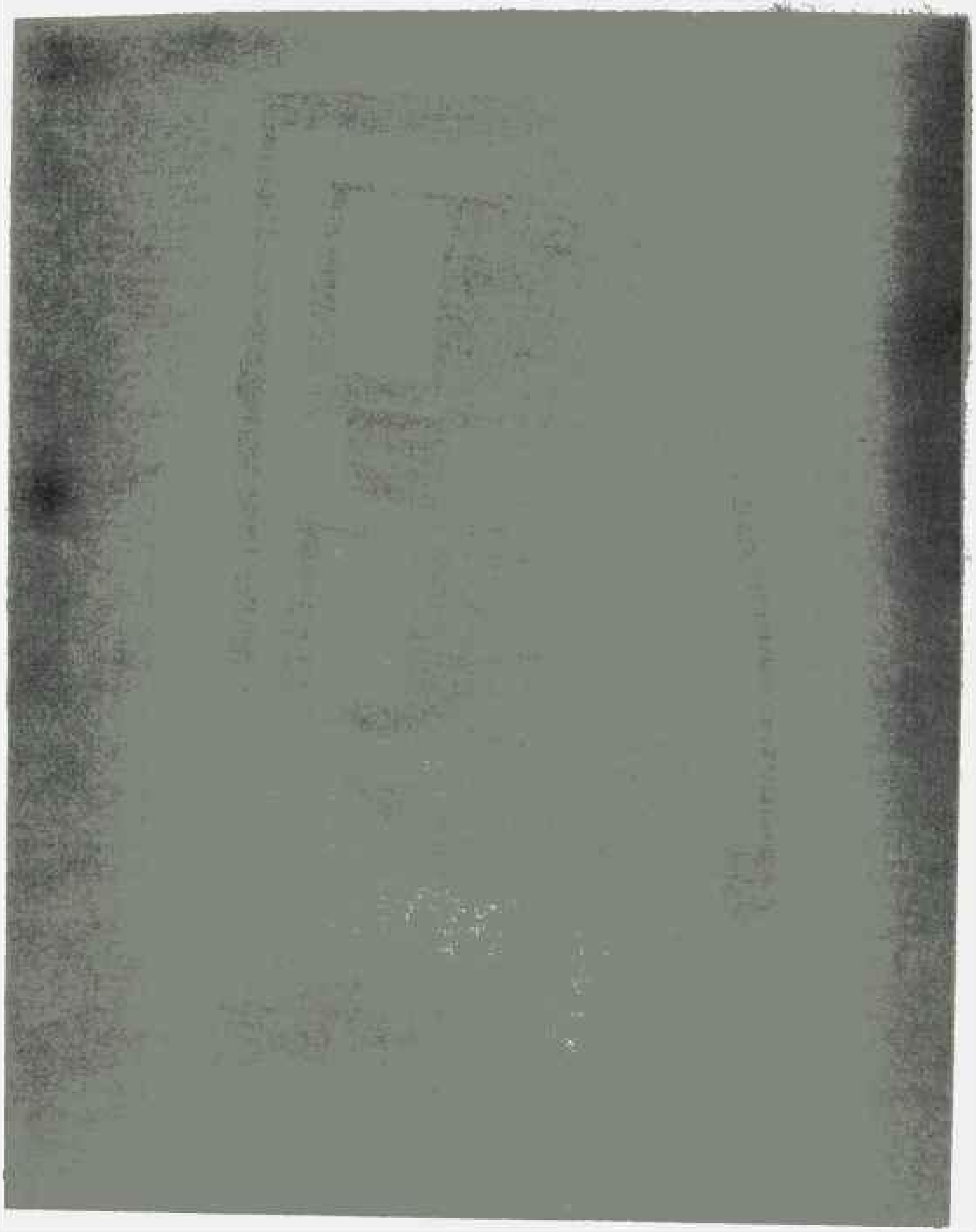
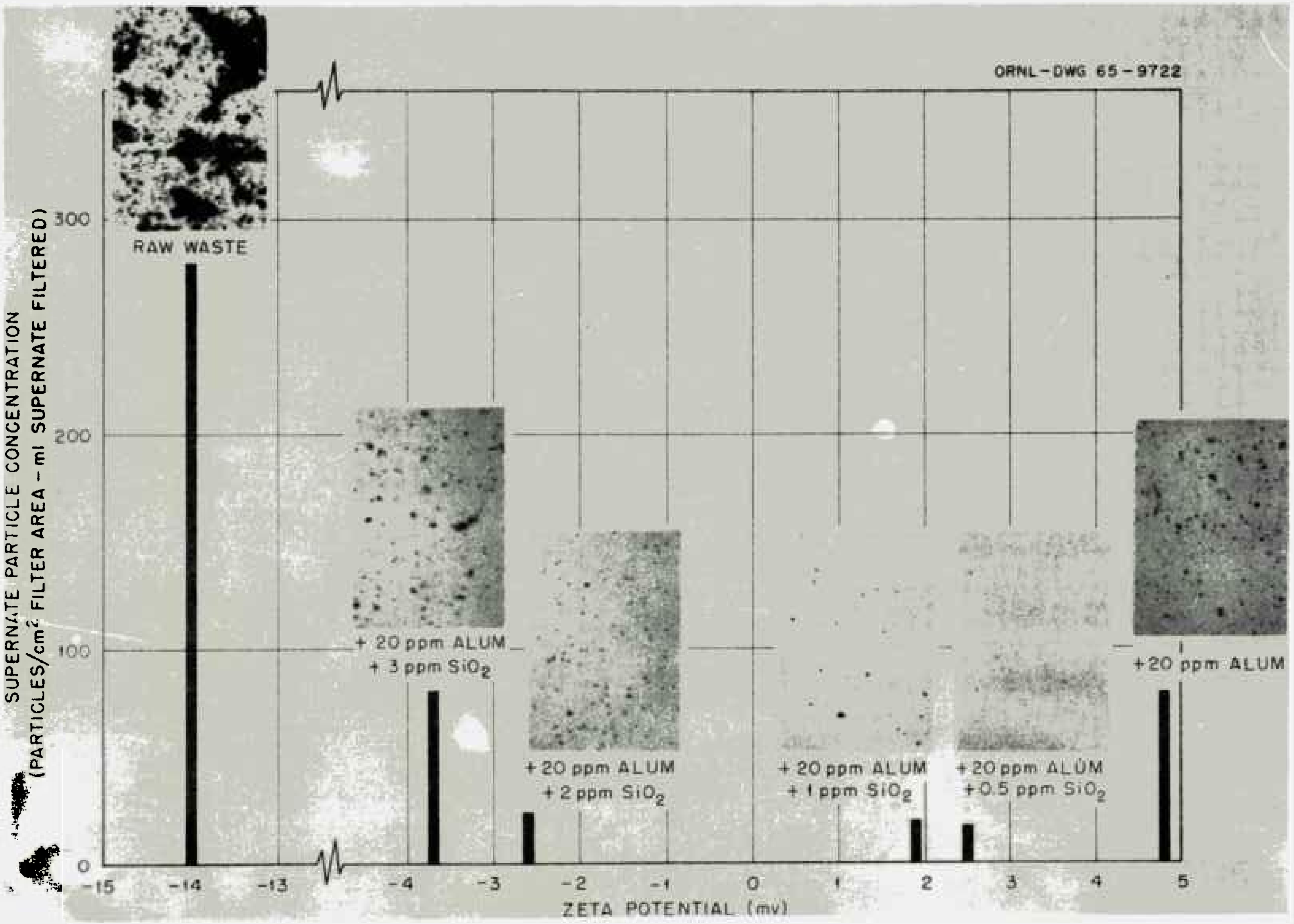



ORNL-DWG 65-9722
SUPERNATE PARTICLE CONCENTRATION
(PARTICLES/cm² FILTER AREA - ml SUPERNATE FILTERED)
300
200
100
0
RAW WASTE
+ 20 ppm ALUM
+ 3 ppm SiO₂
+ 20 ppm ALUM
+ 2 ppm SiO₂
+ 20 ppm ALUM
+ 1 ppm SiO₂
+ 20 ppm ALUM
+ 0.5 ppm SiO₂
+ 20 ppm ALUM
-15
-14
-13
-4
-3
-2
-1
0
1
2
3
4
5
ZETA POTENTIAL (mv)

TREATMENT OF LOW-LEVEL LIQUID WASTES BY ION EXCHANGE

R. E. Blanco

Ion exchange has been widely used in nuclear industry from the earliest inception of the program. Ion exchange is used to demineralize the waters used for the reactor coolants, an operation similar to that in many industries. It is also used to decontaminate the used reactor waters and also many other types of low-level radioactive wastes formed in the nuclear industry.

The principal advantages of ion exchange are: (1) simple equipment, (2) high volume reduction factors, and (3) high decontamination factors. It is best suited for use with wastes that do not contain colloidal materials or high concentrations of solids. Consequently, it is often used as a second step after the waste has been clarified by filtration or flocculation.

PRINCIPLES OF ION EXCHANGE

Ion exchange, as the name implies, is merely the exchange of ion that occurs across the boundary between a solid particle and a liquid. If it is assumed that R represents the insoluble matrix of an exchanger, typical cation-exchange reactions are:

$$2NaR + CaCl_2\ (aq.) \rightleftharpoons CaR_2 + 2NaCl \qquad (1)$$

$$2HR + {}^{90}Sr(NO_3)_2\ (aq.) \rightleftharpoons {}^{90}SrR_2 + 2HNO_3 \qquad (2)$$

Typical anion exchange reactions are:

$$2RCl + Na_2SO_4\ (aq.) \rightleftharpoons R_2SO_4 + 2NaCl \qquad (3)$$

$$RCl + Na\,{}^{131}I\ (aq.) \rightleftharpoons R\,{}^{131}I + NaCl \qquad (4)$$

Equation (2) describes the removal of ^{90}Sr from waste by ion exchange; H^+ ion from the solid exchanger HR are replaced by $^{90}Sr^{2+}$ ions from the waste solution. Complete conversion of the HR to the $^{90}SrR_2$ from can be accomplished by treatment of a sufficient excess of the ^{90}Sr waste solution. An exchanger in this state is termed "exhausted."

It can be "regenerated", however, to the original HR from by reversing the indicated reaction. During regeneration, the concentrated $^{90}Sr(NO_3)_2$ solution can be recovered for disposal as such or for further treatment by other means.

The ion exchanger can be compared to a sponge – the ions can move freely in and out but will be concentrated on the active sites according to certain physical attractions. The number of sites holding on exchanging ions per unit weight of exchanger determines the **capacity** of the exchanger. On the weight basis, it is expressed as milliequivalents per gram. This refers to dry exchanger in the H^+

or Cl^- form. It is necessary to indicate the reference state since the weight will vary with the nature of the ions initially saturating the exchange sites. On a volume basis, capacity is expressed as milliequivalents per millilitre.

TYPES AND STRUCTURE OF ION EXCHANGE MATERIALS

A variety of ion exchange materials are available indicating natural inorganic and synthetic inorganic and organic materials.

For commercial value they should have

a) A large surplus framework electrical charge per unit weight or per unit volume. This is the total exchange capacity and is expressed in terms of milliequivalents of exchangeable ion per gram of dry resin or per millilitre of wet resin.

b) The surplus framework charge must be accessible to ions in solution. This feature in an indication of the porosity of the exchanger.

c) Exchanger pores must be of sufficient size to admit common ions as H^+, Na^+, K^+, Ca^+, Mg^+, OH^-, Cl^-, NO_3^-, SO_4^{2-}, etc. in hydrated form.

d) The exchanger must be of material which is physically and chemically durable over a wide range of conditions.

e) The exchanger must be available in a useful form. Optimum range of particle size for the particle type of material has been found by operational use to be 0.3 to 1.20 mm.

SLIDE 1 Inorganic Ion Exchange Materials (69-9181)

a) Only the zeolites meet most of the aforementioned requirements for commercial exchangers and have been marketed on a large scale. Humus, lignites, coals, straw, and wood have been investigated thoroughly in certain areas for use in treatment of radioactive waste. Relatively low exchange capacity is offset by low cost, availability, and ease of incineration of spent materials. Zeolites are crystalline alumina-silicates belonging to the subclass tektosilicate of the class silicate.

b) The zeolite framework is open and wide-meshed with cavities containing cations to balance the negative charge of the framework. Pore sizes are very uniform and rather small, providing a "sieving" action as mobile ions are exchanged. Larger ions are excluded from exchange, the maximum size being dependent upon the particular zeolite. The zeolite framework $(Si, Al)O_2$ is held together by strong bonds and is very rigid. Water molecules can be removed without affecting the stability of the structure. The name "zeolite", in fact, is derived from the Greek and means "to boil", referring to the apparent boiling that occurs when these minerals are heated and the water is released.

c) Vermiculite and illite are also alumino – silicates (class phyllosilicates) and have been used to sorb Cs from wastes.

d) A number of synthetic alumino – silicates and phosphates and salts of Zr, etc., are available in well characterized form and are specific for sorbing certain ions; for example, a ferro cyanide sorbs Cs effectively.

SYNTHETIC ORGANIC RESINS

SLIDE 2 Strong Acid or Strong Base Ion Exchange Resins (69-8608)

a) **Cation-exchange resins** — Most of the cation-exchange resins commonly used in waste treatment are addition polymers made by sulphonation of a styrene divinylbenzene copolymer. Sulphonic acid groups are introduced after polymerization by heating with concentrated sulphuric acid or chlorosulphonic acid. Commercial divinylbenzene (DVB) is generally used as the crosslinking agent. Ratio of DVB to styrene is easily adjusted in the reaction and therefore control of degree of crosslinking, which in turn determines porosity, is simple. Reproducible results are achieved with relative ease.

Nominal DVB content, as mentioned in manufacturers'literature, refers to mole percent of pure divinylbenzene. Commonly used resins containing 8 to 12% DVB resins have been made available. Increasing DVB content decreases swelling and porosity and increases toughness and mechanical stability. The opposite happens as DVB content decreases. Low DVB content resins swell strongly and are soft and gelatinous.

b) **Anion-exchange resins** — Synthesis of anion-exchange resins by the addition reaction is very similar, to a point, to preparation of the cation exchangers. Beads formed by suspension copolymerization of styrene and DVB are treated with chloromethyl ether catalyzed by aluminum chloride or zinc chloride. $-CH_2Cl$ groups are introduced on the benzene rings. This product is then aminated with trimethylamine to provide a highly ionized functional group of quaternary ammonium.

The resin is a strong-base anion exchanger and in the OH^- form has the basicity of NaOH. Methylstyrene, vinylanisole and other styrene derivatives can be used with crosslinking agents other than DVB, such as vinylacrylate.

c) Weak acid resins often have a phenol-foraldehyde-condensation polymeric base and contain phenolic (OH) and/or carboxylic groups attached to the benzene rings. These resins are only useful at high pH values where they are ionized and exchange can occur. As we will mention later, the phenolic group holds Cs very tightly.

d) Weak anion resins contain primary ($-NH_2$) or secondary (-NH-) amine groups on a polymeric base.

SLIDE 3 Controlling Factors in Ion Exchange (69-9180)

SELECTIVITY

The selectivity, the ability of an exchanger to sorb one ion in preference to another, is a very complex function. Normally, it is not necessary for a waste or fuel processing plant operator to determine the relative selectivities. Most are listed in tables in the literature — often by manufacturers.

SLIDE 4 Definition of Distribution Coefficient and Separation Factor (69-9183)

a) $K_{\frac{Cs}{Na}} = \dfrac{(CsR)_R(Na^+)_S}{(Cs^+)_S(Na)_R}$ = Selectivity Coefficient

K and Kd are essentially constant where Cs is present in trace amounts and the concentration of Na in the exchanger and solution is essentially constant. This is the normal condition where separating trace radioisotopes from each other or from the macro ions. The selectively constant varies when macro amounts of both ions are present. Most selectivity constants can be found in the literature.

Selectively coefficients can be calculated when the experimental conditions are known. The variables involved include the swelling pressure, the partial molar or molal volumes of ions in resins and solution phases and the activity coefficients of the ions in the two phases. All of this information is readily available or can be computer except the value of the activity coefficient of the ions in the ion exchanger or resin phase. This value can be determined by empirical methods.

SLIDE 5 Relative Affinities of Ions for a Strong Acid Resin with Varying Percentages of Crosslinking (69-9176)

Based on selectivity coefficients, this slide presents the relative affinities of certain monovalent and divalent cations for a strong-acid sulphonated styrene-divinylbenzene resin, Duolite C-20. The affinity for the hydrogen ion was arbitrarily taken as one.

SLIDE 6 General Limitations of Ion Exchange (69-9175)

a) Radionuclides in the waste must be ionized and exchangeable.

b) Concentration of suspended solids must be very low. Such material clogs exchange columns, coats exchange materials and hampers backwashing and regeneration.

c) Concentration of total solids should be less than 2500 mg/liter and preferably below 1000 mg/liter. It is generally uneconomical to rapidly exhaust available exchange capacity with non-radioactive ions.

d) Radionuclides which are mono-valent or of low atomic number are difficult to remove from solution by ion exchange unless an exchange material with a high specificity for the element can be found.

e) Certain radioelements are chemically very complex, and efficient removals from waste streams generally cannot be guaranteed without somewhat extensive pretreatment.

SLIDE 7 Limitations of Inorganic Exchangers (69-9174)

The most widely used exchangers, the synthetic organic resins have a large number of excellent characteristics which make them highly suitable for waste treatment. However, they have certain limitations.

SLIDE 8 Limitations of Synthetic Organic Resins (69-9182)

The radiation and heat limitations are not particularly significant in treating low- and intermediate-level wastes. High-level wastes are never routinely treated by ion exchange as a waste treatment method.

SLIDE 9 Capacities of Typical Exchangers (69-9184)

a) All of the physical data on each resin is available in catalogues (see IAEA Technical Series Book 78).

b) Most of the resins made in various countries are very similar by types.

c) The inorganic exchangers have a density of about 3.0 compared to about 1.0 for the resins. Also, the resins swell when they absorb water and ions-swelling is a function of degree of crosslinkage. Therefore, direct comparisons on the basis of capacity are complex.

d) The outstanding criteria for choosing a resin is probably (1) specificity for particular radionuclides; i.e., will it do the job? , and (2) cost and operating characteristics.

ION EXCHANGE EQUIPMENT

Ion exchange can be conducted in a series of batch operations where the solution successively contacts fresh exchanger. Generally, it is much more efficient to use columns of exchangers. Almost all operating plants use fixed-bed columns. A few use countercurrent or continuous countercurrent column units.

The system of column operation has a number of variations. These include:

1) **Single column, fixed bed**

    a) Cation exchange only
    b) Anion exchange only
    c) Monobed or mixed bed

2) **Series columns, fixed bed**

    a) Cation-exchange columns in series
    b) Anion-exchange columns in series
    c) Mixed bed columns in series

3) **Dual columns, fixed bed**

    a) Cation-exchange columns
    b) Series columns of (a)

4) **Moving bed, continuous countercurrent exchanger or pulsed-bed contactor**

    a) Cation-exchange columns
    b) Anion exchanger

5) **Centrifuge lined with exchanger**

    a) Cation exchanger
    b) Anion exchanger

SLIDE 10 Fixed Bed Ion Exchange, Single Column (69-9625)

SLIDE 11 Typical Columns (photo 56219)

SLIDE 12 Mixed Bed Ion Exchanger (69-9620)

SLIDE 13 Schematic of a Continuous Countercurrent Exchanger (69-9599)

SLIDE 14 Commercial Countercurrent Ion Exchange Unit (Photo 96822)

Location: Manitoba, Canada

Application: Demineralization for Industrial

Dimensions: Each unit overall: 8 ft x 8ft x 25ft; Loading sections: 36 in. diameter; Regeneration sections: 24 in. diameter

Materials: Rubber lined steel, 304 and 316, stainless steel

Capacity: 220 gallons per minute (310,000 gallons per day). Reducing 1125 ppm total dissolved solids to less than 3 ppm

SLIDE 15 Breakthrough Curves (65-907A)

Columns are controlled by continuously monitoring the concentration of ions in the effluent. This slide shows a plot of the log of the fraction (C/Co) of ions coming through the column vs the column volumes of liquid treated (C = effluent concentration; Co = original concentration). When the effluent concentration reach a predetermined value (DF), the column is exhausted and the flow is stopped. It is then regenerated (back flow) with concentrated acid or base if the unit is operating on a demineralization cycle to remove all cations or anions. This mixed bed (cation and anion) unit indicates exhaustion by an increase in conductivity on the effluent water and thus indicates that the radionuclides will break through soon. This unit shows the following DF's: ^{144}Ce – 85; ^{60}Co – 72; ^{137}Cs – 510; ^{106}Ru – 440; ^{95}Zr-Nb – 8.6; ^{90}Sr – 6300, as measured separately but indicated by Ca^{+2} breakthrough.

SLIDE 16 Leakage and Capacity Data for Na-H Cycle of a Sulfonic Cation-Exchange Resin (69-9600)

As mentioned previously, the capacity of resins as listed by the manufacturers is the total capacity. Utilization of total resin capacity is somewhat difficult and usually uneconomical since a large excess of regenerant is required. This slide illustrates the increase in capacity of a cation exchange resin as the quantity of acid used in regeneration is increased. It can be noted that at the upper end of the curve a large increase in quantity of regenerant produces a relatively small gain in resin capacity. Curves such as this are normally available from the manufacturer of the resin as they must be determined for specific resins and regenerants.

Resins used for the removal of radioactive cations are usually operated in the $H^{\pm}$ cycle and regeneration is accomplished with the strong mineral acids, sulfuric, hydrochloric or nitric. NaOH or NaCl are used for regeneration of anion exchangers.

Almost all nuclear establishments use ion exchange as part of their treatment system. We will look at specific installations later.

SLIDE 17 Schematic – Natural Zeolite (Clinoptilolite) Treatment Plant, Idaho Falls, USA (69-10009)

In one application of ion exchange at Idaho Falls, large volumes of water from a storage basin for irradiated fuel elements are routinely processed through mineral exchangers. The contaminated water contains 0.5 mg/liter chlorine for sterilization purposes and 200 mg/liter sodium nitrate for corrosion control. Small amounts of calcium and magnesium ions are present and the pH of the water is about 8.2. Principal radioactive contaminants are ^{90}Sr and ^{137}Cs.

Four paralell sets of two ion exchange columns in series provide the only treatment the wastes receives. The columns are standard 200-liter mild steel drums filled with a 60-cm depth each of the zeolitic mineral clinoptilolite. When the bottom drum is exhausted as determined by increasing radioactivity, it is removed and used as number one column in a new two-unit series. The number one column which is replaced is capped, sealed, and buried as solid waste. The total life of each drum is 800 column volumes. The average decontamination factor achieved has been approximately 200.

SLIDE 18 Synthetic Zeolite Ion Exchange, Savannah River, USA (69-10010)

Typical Decontamination Factor	200
Volume of Zeolite	284 liters
Useful Capacity	4000 bed volume

REFERENCES AND EXCERPTS FROM:

1. L. A. Emelity, "Treatment of Radioactive Liquid Wastes by Ion Exchange," Regional Training Course on Radioactive Waste Management, Rio de Janeiro, Brazil (1968).

2. *Operation and Control of Ion-Exchange Processes for Treatment of Radioactive Wastes*, IAEA, Technical Reports Series Nº 78 (December 1967).

INORGANIC ION EXCHANGE MATERIALS

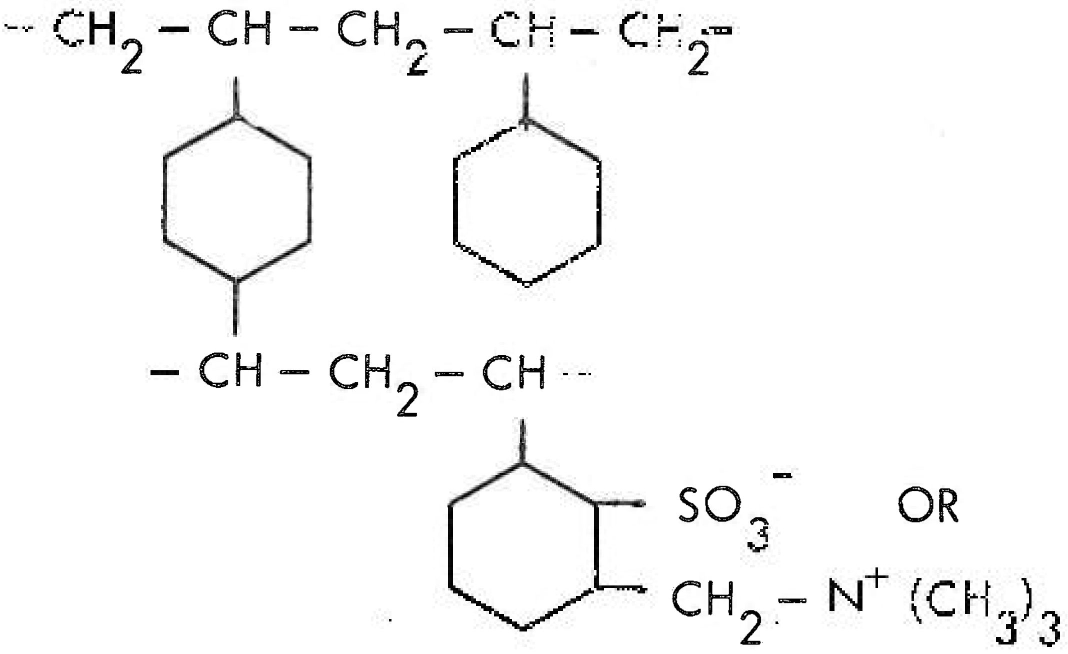
CLAYS

- Attapulgite
- Halloysite
- Kaolinite
- Illite
- Montmorillonite
- Vermiculite

ZEOLITES

- Analcite
- Chabazite
- Clinoptilolite
- Harmotome
- Heulandite
- Natrolite
- Sodalite

STRONG ACID OR STRONG BASE ION EXCHANGE RESINS



Copolymer of Styrene - Divinylbenzene

CONTROLLING FACTORS IN ION EXCHANGE

1. Exchanger capacity
2. Degree of crosslinking (extent of inter-connection of polymers in synthetic organic resins)
3. Concentration of the solution
4. Ionic valences
5. Ionic sizes
6. Swelling pressure
7. Sieve action
8. Interactions between the mobile ions
9. Solution temperature
10. Interactions between mobile and fixed ions in the exchanger
11. Selectivity

DEFINITION OF DISTRIBUTION COEFFICIENT AND SEPARATION FACTOR

$NaR + CsCl \rightleftarrows CsR + NaCl$ Cation Exchange (R = exchanger)
$RCl + NaOH \rightleftarrows ROH + NaCl$ Anion Exchange

$$\text{Distribution Coefficient} = Kd(Cs) = \frac{\text{wt Cs/g exchanger}}{\text{wt Cs/cm}^3\text{ solution}}$$

$$\text{Separation Factor} = K_{(Cs/Na)} = (Cs/Na)_{\text{solution}} / (Cs/Na)_R$$

Examples of Complexes: cation Pu^{+4}; Anion $Pu(NO_3)^{-n}_{(4+n)}$

UO_2^{+2}; $UO_2(CO_3)_3^{-4}$

RELATIVE AFFINITIES OF IONS FOR A STRONG ACID RESIN WITH VARYING PERCENTAGES OF CROSSLINKING

Monovalent	x-4	x-8	x-12	x-16
H	1.0	1.0	1.0	1.0
Li	0.90	0.85	0.81	0.74
Na	1.3	1.5	1.7	1.9
Cs	2.0	2.7	3.2	3.45
Ag	6.0	7.6	12.	17.
Divalent				
Mn	2.2	2.35	3.5	2.7
Co	2.65	2.8	2.9	3.05
Ca	3.4	3.9	4.6	5.8
Sr	3.85	4.95	6.25	8.1
Pb	5.4	7.5	10.1	14.65

GENERAL LIMITATIONS OF ION EXCHANGE

1. Radionuclides in the waste must be ionized and exchangeable.
2. Concentration of suspended solids must be very low.
3. Concentration of total solids should be less than 2500 mg/l and preferably below 1000 mg/l.
4. Radionuclides which are mono-valent or of low atomic number are difficult to remove.
5. Certain radioelements are chemically very complex.

LIMITATIONS OF INORGANIC EXCHANGERS

1. Relatively low exchange capacity.
2. Zeolites are difficult to size.
3. Relatively low resistance to acids and alkalies.
4. Many have limited stability in solutions of very low silica or salt content.
5. The zeolites have relatively low resistance to abrasion.

LIMITATIONS OF SYNTHETIC ORGANIC RESINS

1. Relatively high cost
2. Limited stability to heat
3. Limited radiation stability

Percent capacity loss at 10^9 R	
Strong acid	10
Weak acid	100
Stong Base	40
Weak Base	20

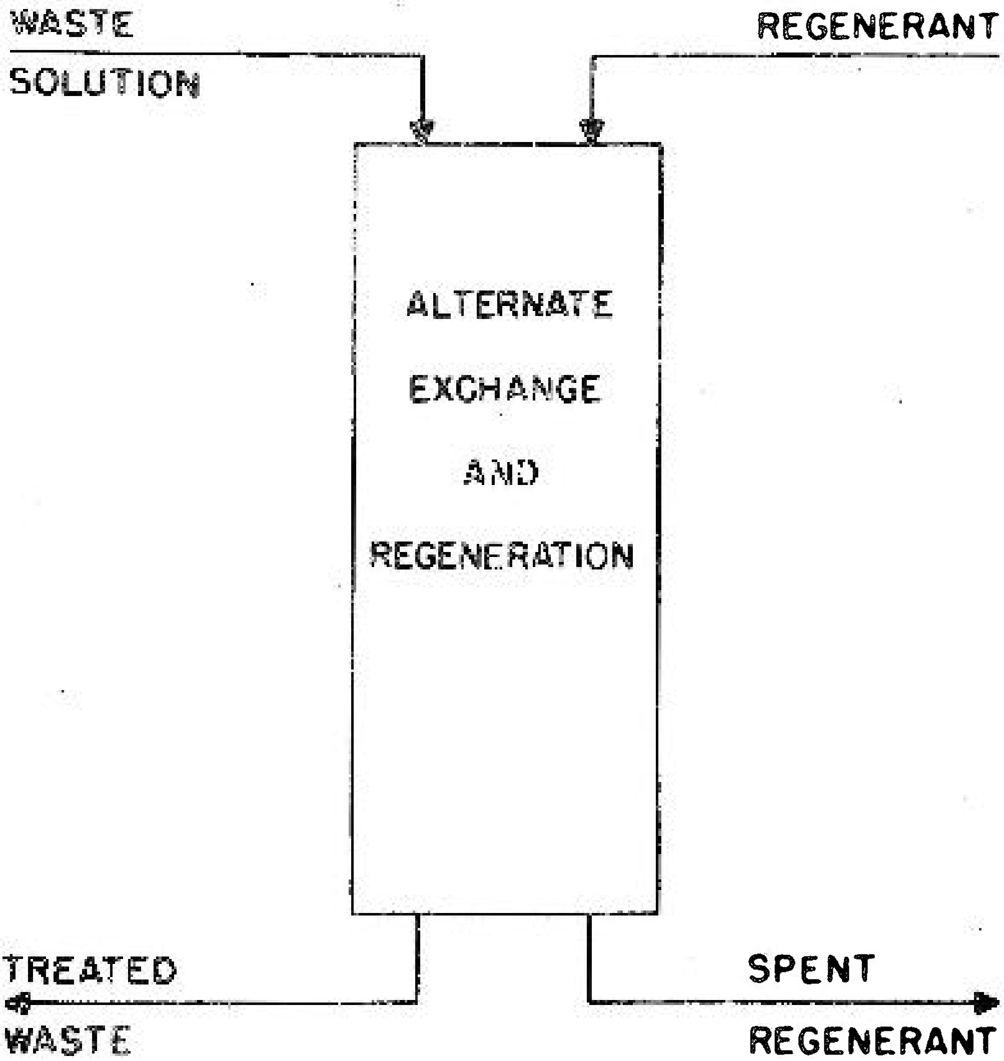
LIMITATIONS OF SYNTHETIC ORGANIC RESINS

1. Relatively high cost
2. Limited stability to heat
3. Limited radiation stability

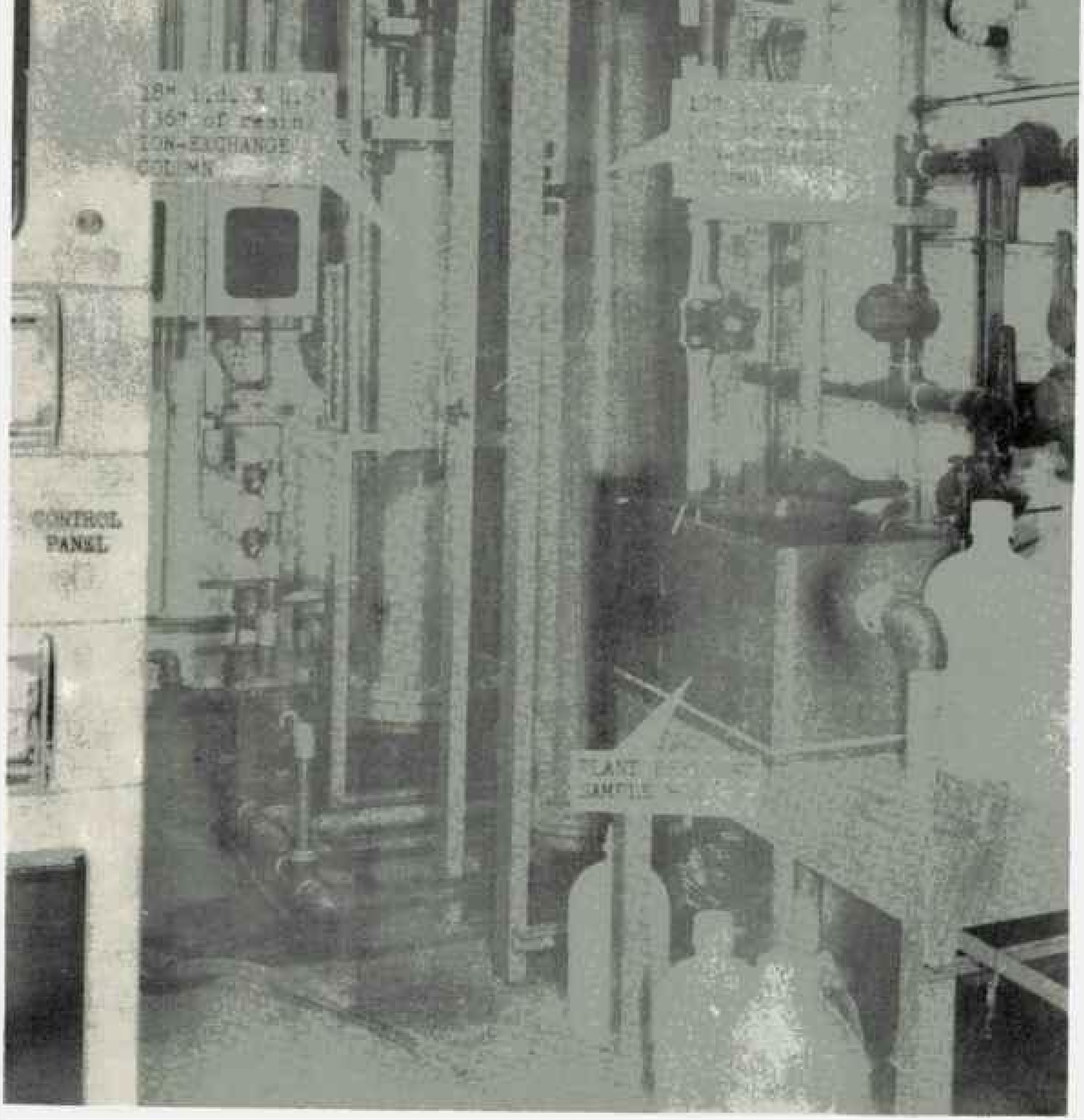
Percent capacity loss at 10^9 R	
Strong acid	10
Weak acid	100
Stong Base	40
Weak Base	20

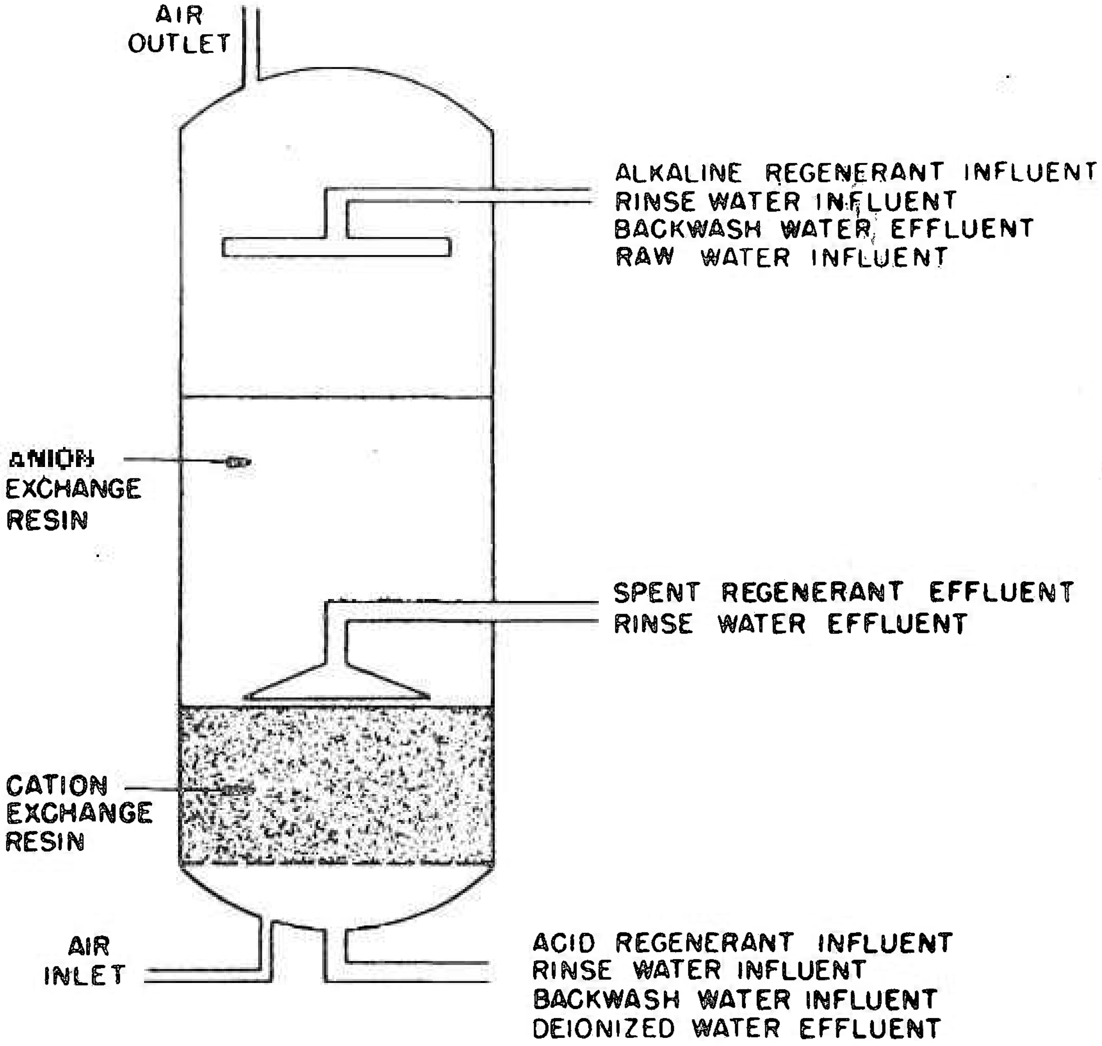
CAPACITIES OF TYPICAL EXCHANGERS

		Inorganic		meq/g	meq/
	Decalso	Permutite Co.,	USA	1.4	-
	Doucil	J. Crosfield,	UK	1.2	-
	4A	Linde,	USA	5.3	-
	Zeolon	Norton	USA	1.9	-
		Organic			
Cation	Dowex 50-X8	Dow,	USA	4.8	1.9
	Dowex 50-X12	Dow,	USA	-	2.1
	Ku-2-8	NIIP,	USSR	4.7	
Anion	Amberlite IRA-400	Rohm & Haas,	USA	3.7	1.4
	Amberlite IRA-900	Rohm & Haas,	USA	4.4	1.0
	AV-17-6	NIIP,	USSR	4.3	-

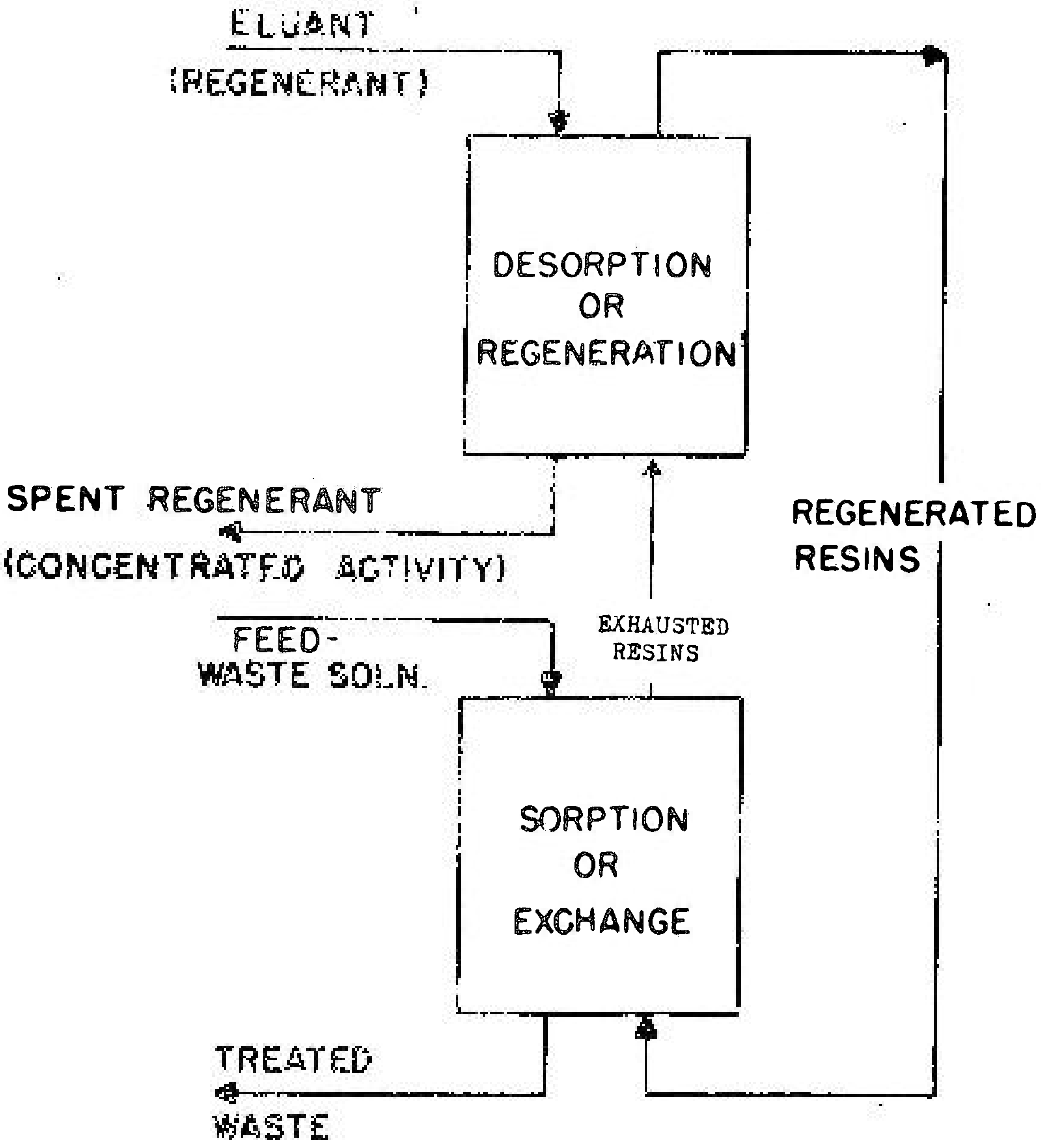


FIXED BED ION EXCHANGE
SINGLE COLUMN

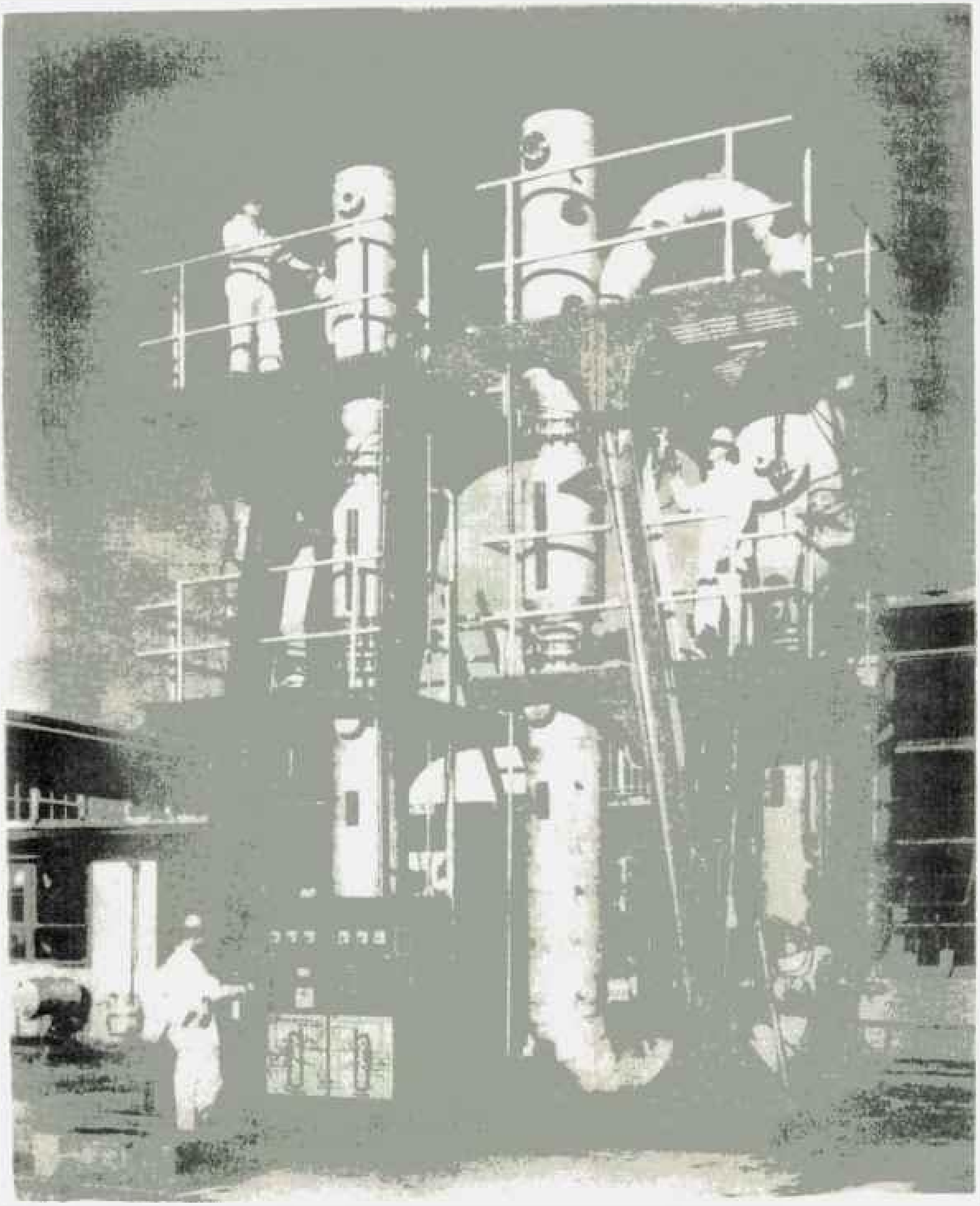

18" I.D. x 11.5'
136" of resin
ION-EXCHANGE
COLUMN
CONTROL
PANEL
PLANT
SAMPLE

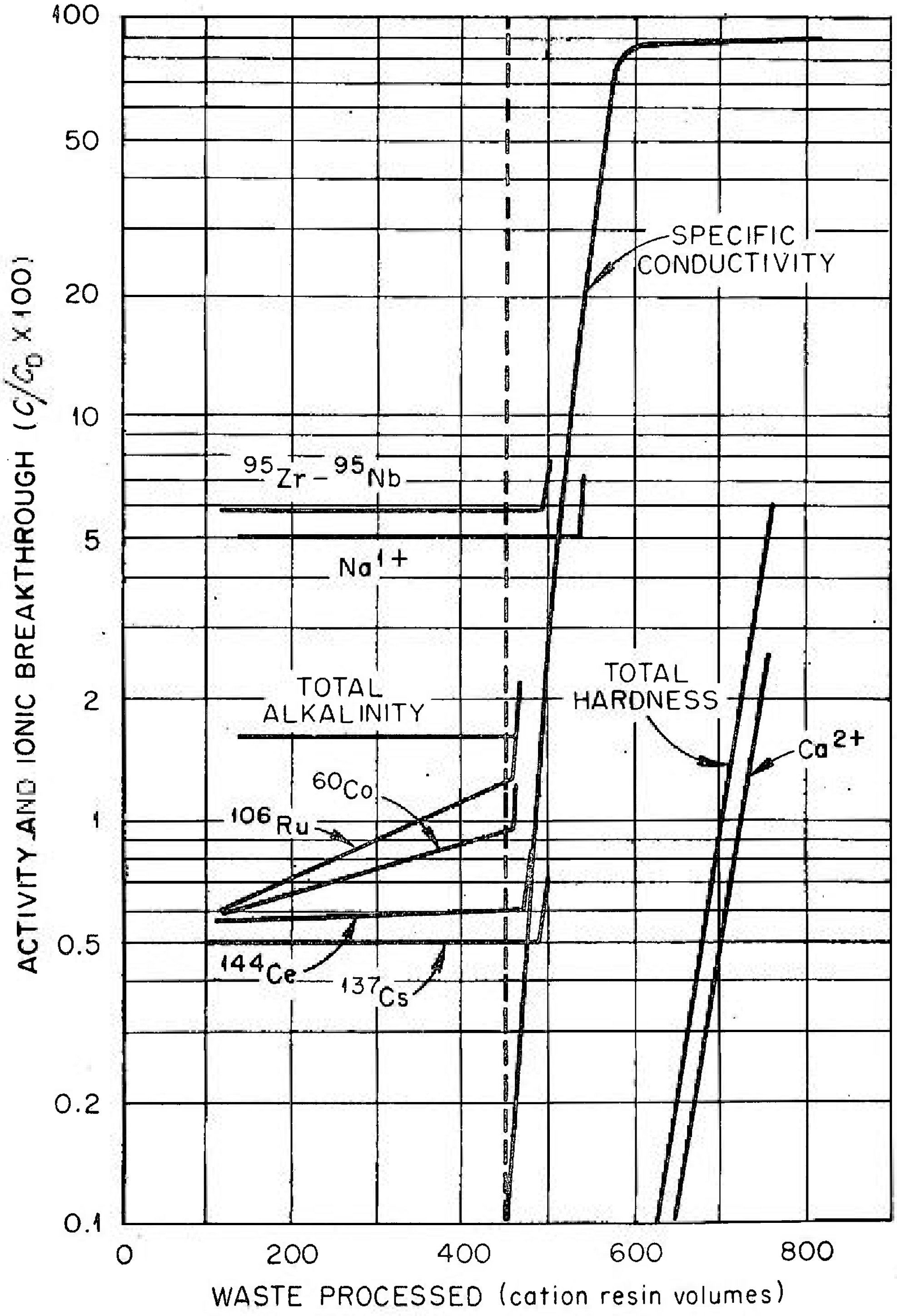


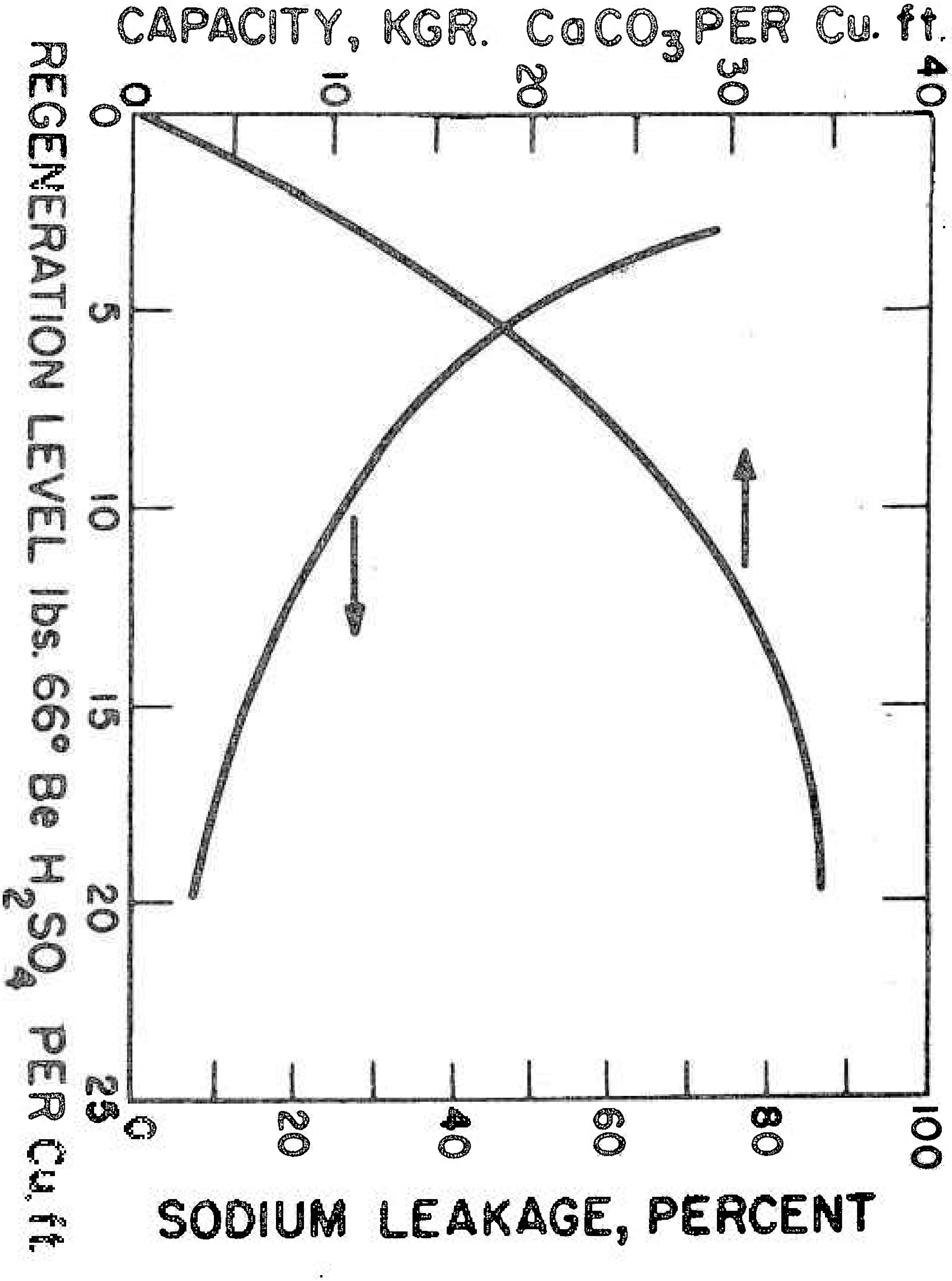
MIXED BED ION EXCHANGER



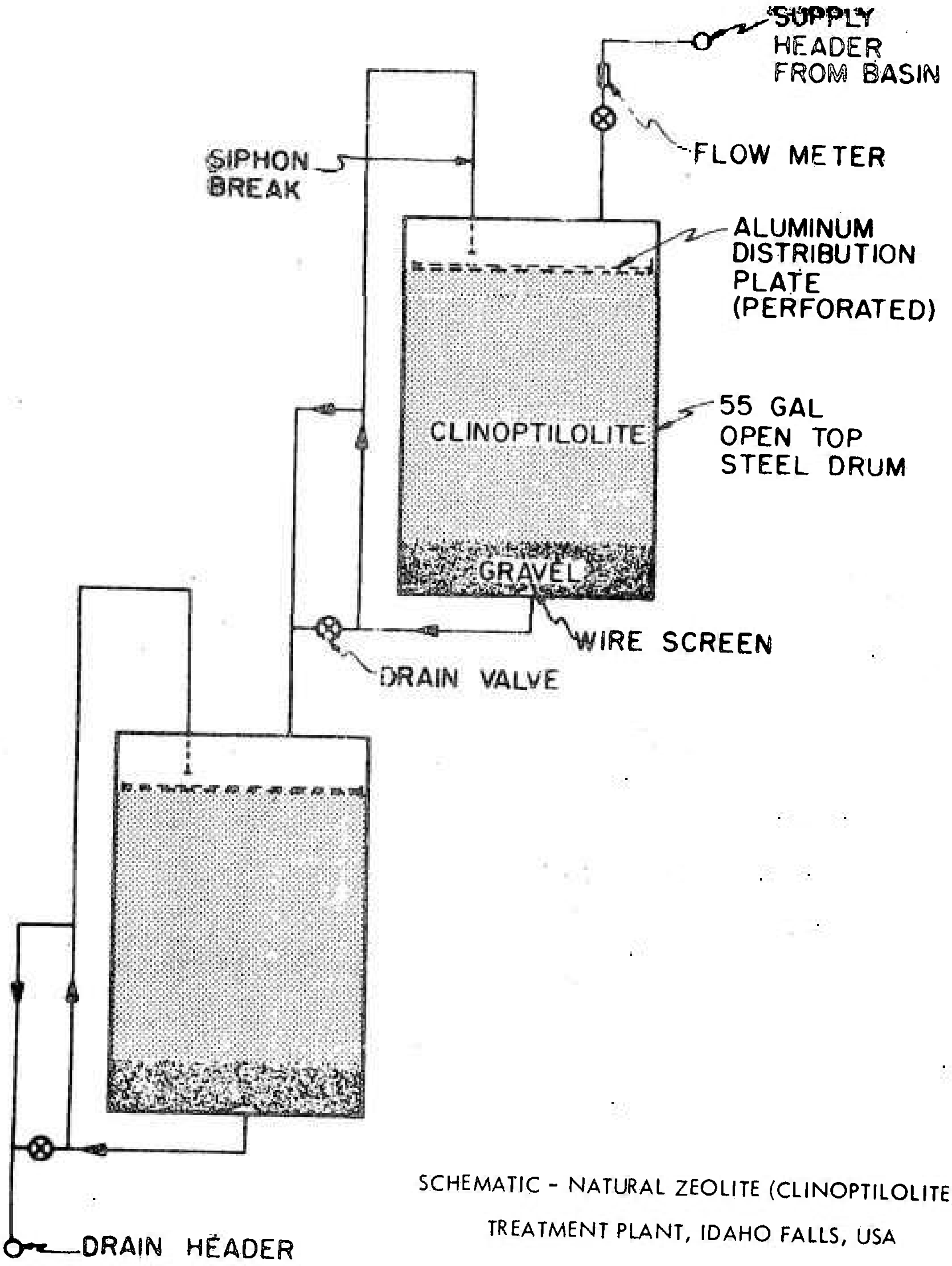
SCHEMATIC OF A CONTINUOUS COUNTER-CURRENT EXCHANGER



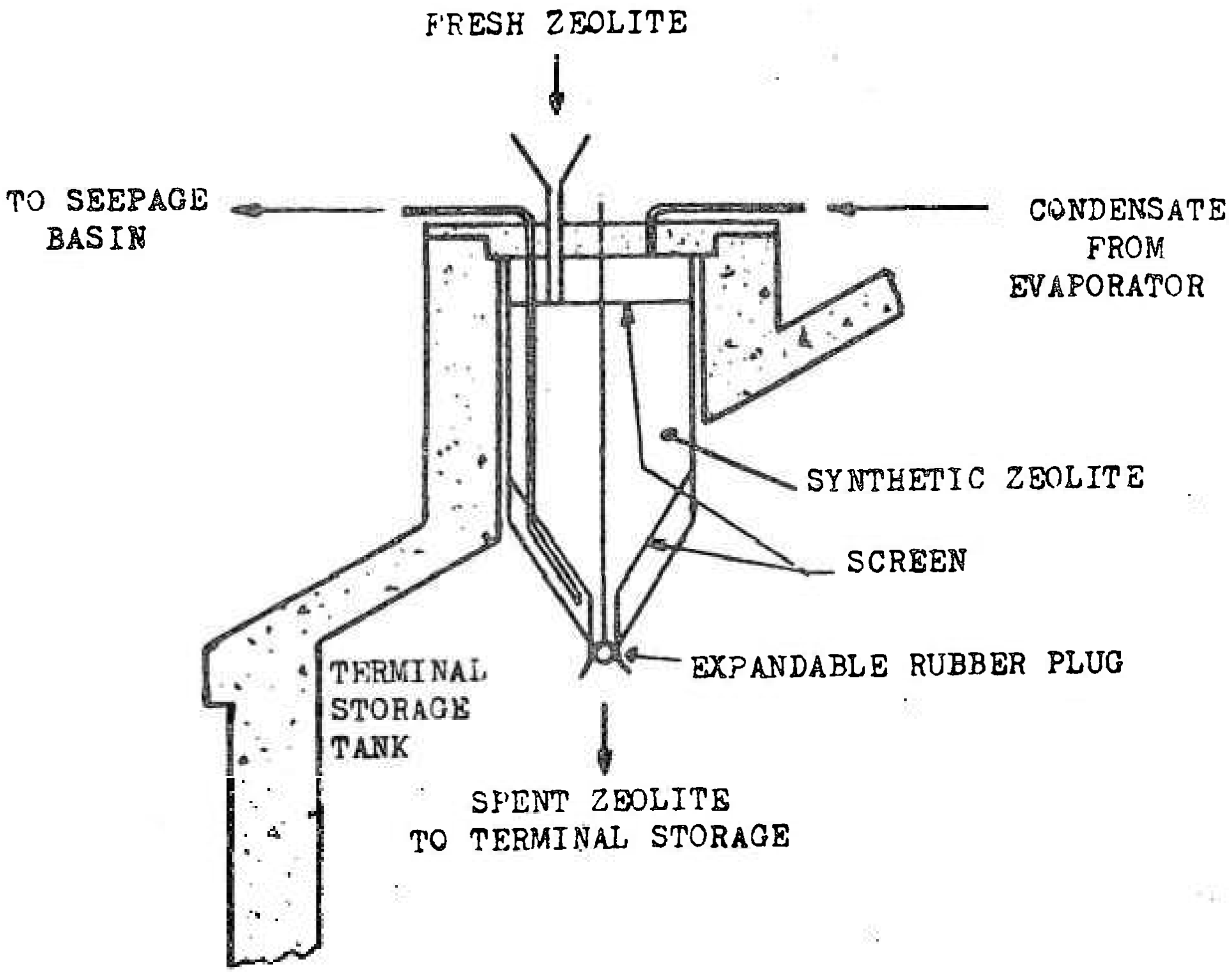

100
50
20
10
5
2
1
0.5
0.2
0.1
ACTIVITY AND IONIC BREAKTHROUGH (C/C₀ X 100)
0
200
400
600
800
WASTE PROCESSED (cation resin volumes)
SPECIFIC CONDUCTIVITY
95Zr – 95Nb
Na1+
TOTAL ALKALINITY
TOTAL HARDNESS
Ca2+
60Co
106Ru
144Ce
137Cs



LEAKAGE AND CAPACITY DATA FOR Na-H CYCLE OF A SULFONIC CATION-EXCHANGE RESIN



SCHEMATIC - NATURAL ZEOLITE (CLINOPTILOLITE) TREATMENT PLANT, IDAHO FALLS, USA



SYNTHETIC ZEOLITE ION EXCHANGE, SAVANNAH RIVER, USA

TREATMENT OF LOW-LEVEL LIQUID WASTES BY EVAPORATION

R. E. Blanco

Evaporation is one of the most commonly used methods in the chemical industry, and it is also very effective for removing radioactive materials from liquid effluents. Evaporation is generally applied to the treatment of medium – and high-level wastes and in the cases where a high decontamination factor is required, or where the waste is otherwise not suited for processing by alternative techniques. Compared with chemical treatment and ion-exchange, capital costs are high but provided the processing capacity is fully utilized the costs per unit volume are generally not excessive.

Low-level wastes are generally very large in volume and contain a low concentration of salt. Therefore, the cheaper chemical treatment methods are generally used for these wastes. However, a few installations are willing to pay the extra costs to obtain a simpler system to operate and a higher decontamination factor.

On the average, a decontamination factor of more than 10^4 between condensate and thick liquor can be achieved. In many cases a factor of 10^6 has been reached and sometimes even 10^7 or more. However, these figures may be reduced by the presence of volatile radioactive materials or owing entrainment and foaming.

The maximum volume reduction which can be achieved depends upon the amount and the properties of dissolved solids in the waste. The limiting factors are the crystallization of dissolved solids at the colder part of the evaporator, foaming, scaling, and corrosion. Volume reduction is not usually restricted by the presence of small amounts of suspended solids, but higher volume reduction results in higher activity in the thick liquor and necessitates more substantial biological shielding in the plant. It also results in greater concentrations of activity in the distillate.

TYPES OF EVAPORATORS

Evaporation is a common unit operation and the details of evaporator technology are studied in other engineering courses. Here, we wish to emphasize the effect that the presence of radionuclides has on the choise of the evaporator type. The big considerations are the cost of remote maintenance and the capital cost of the massive shielding that is required for high-level wastes.

SLIDE 1 Factors in Choise of Evaporator Type (69-9167)

SLIDE 2 Evaporator Types (69-9166)

Coil or pot type

SLIDE 3 Chalk River Coil Evaporator (69-9623)

This type of evaporator is now seldom used in the chemical industry, but in processing radioactive wastes it is frequently used especially for small installations. Even in a big laboratory, for instance at Chalk River, this type of evaporator has been used since 1958 for the processing of low-activity wastes. This slide illustrates the simplified flowsheet of the Chalk River evaporator constructed of type 347 stainless steel. The evaporator has a hold-up volume of 900 liters and a throughput rate of 900 liters per hour. A 91-cm diameter column containing two deentrainment devices surmount the evaporator. The first device is an impigement plate and the second is a wire-mesh demister unit.

Pot-type evaporators are simply constructed and may be useful for simple batchwise evaporation. In the United States, even at big power reactor stations, pot-type evaporators ranging in capacity from 2.7 to 45.4 liters/min have been operated on a batch basis with a distillate-to-concentrate ratio between 10 to 1 and 50 to 1.

SLIDE 4 ORNL Intermediate-Level Waste Evaporator (63-2857)

A 600-gallon-per-hour semi-continuous evaporator for concentrating intermediate-level (10^{-5} to 10 curies per gallon) radioactive waste is operated at the Oak Ridge National Laboratory. The evaporator installation cost about $1,000,000.

The waste operator with its auxiliary equipment is located in two underground cells of a special building under construction near the central waste tank farm. The general arrangement of these cells is shown in this slide. Shielding for the evaporator and feed tank cell (dimensions 14 x 26 x 20 ft) is five feet of concrete, based on the assumption that the evaporator may occasionally be required to concentrate high-level waste having original specific activity of 2800 curies per gallon. Shielding for the condenser cell (dimensions 12 x 14 x 12 ft) is three feet of concrete, based on the assumption that 10% of the ruthenium-106 in the evaporator might volatilize during evaporation under maloperation. Both cells have stainless steel floors and four-foot high wainscoting on all walls to facilitate decontamination when entrance into the cells is required. Except for pipes and ventilation ducts, the only entrance to the cells is through the roof tops, which are removable for personnel access to the evaporator equipment. A 20-ton gantry crane straddles the cell hatches to lift the heavy hatch covers (concrete slabs) and process equipment during construction and maintenance periods. The crane by is enclosed to provide for a secondary containment zone when the cell hatches are removed, and one end of the bay will contain a vertical sliding door large enough to pass the crane to a loading dock outside.

The evaporator and its auxiliary equipment are type 304 L stainless steel to afford corrosion resistance and to facilitate decontamination. Although the intermediate-level waste is usually alkaline and is normally evaporated in the alkaline state, the laboratory produces some high-activity acid waste, which can be delivered to the evaporator through special stainless steel pipe lines.

The evaporator is a pot, with seven internal coils of 1-1/2-in. schedule-40 pipe to provide heat or to cool the bottoms before they are jetted from the pot. Total heat transfer surface is 570 square feet. The coils are arranged in concentric array in the lower three feet of the vessel, which is 10 ft in diameter by 12 ft tall. Its capacity is 6000 gallons. By means of remotely operated valves, steam or water can be supplied to any coil independently so that a ruptured coil can be isolated from the system without shutting down the evaporator. This design was chosen over a vapor-compression evaporator, a thermal-circulation evaporator with external tube bundle, and a thermal-circulation evaporator with internal steam chest because of lower cost, simpler design, and the fact that fewer welds are exposed to potentially corrosive conditions. The vessel is designed to operate at atmospheric pressure and up to 300°F. The operating volume is 2200 gallons, which means that the starting liquid level will be about 1-1/2 feet above the top coils, and the final level will be about a foot above the coils. Operation is in semibatch fashion, that is, vapors will be drawn off overhead continuously after the vessel is filled to operating level, and feed will be supplied upon the demand of a liquid-level controller until the density of the accumulated bottoms reaches a desired point. Then, the feed and steam will be shut off manually and the bottoms cooled to jetting temperature (below 165°F). The bottoms will be transferred from the vessel by submerged jets similar to the feed tank jets.

Because foaming is expected to be a problem during alkaline evaporations, a steam coil of six spiral turns of one-inch pipe is mounted three feet above the normal liquid level in order to break the foam. The pot also has three spray nozzles aimed toward the liquid surface and capable of being supplied with foam-breaking agents.

Vapor leaving the evaporator pot must pass through an impingement-type entrainment separator suspended in the top head of the pot. This device causes several sudden changes in the direction of vapor flow, changes that cause large entrained liquid droplets and solid particles to be flung against the surfaces of the separator and thus removed from the vapor stream.

A 10-in.-diam pipe conducts the vapor from the top of the evaporator pot to a stainless-steel wire-mesh filter. The filter bed of 0.004-in.-diam wire packed to a density of 15 pounds per cubic foot is four feet in diameter and three feet deep, mounted inside a stainless steel vessel. The function of this vapor filter is to remove micron- and sub-micron-sized entrained liquid droplets from the vapor stream. It is designed to afford a decontamination factor of 1000 across it.

Noncondensible gases pass from the receiver through a caustic scrubber (to be used mainly for acid evaporation) to off-gas filters located in underground chambers outside the building. The gases are then drawn into the ORNL central vessel off-gas system for further treatment and eventual dispersal into the atmosphere from a tall stack.

SLIDE 5 Steam-Jacketed Kettle (69-9621)

In a small installation a jacketed kettle, the simplest pot-type evaporator, may be used. A typical kettle is shown in this slide. To the bottom of the jacket is connected a pipe for condensate outlet and another for discharge of thick liquor from the kettle. Outlets for steam and non-condensed gases are provided near the top of the jacket.

SLIDE 6 Merits and Limitations of Coil and Jacket Evaporators (69-9165)

SLIDE 7 Standard Vertical-Tube Evaporator (69-9622)

The vertical-tube evaporator illustrated in this slide is now widely used. The body is normally a cylinder and the heating surface is provided by short tubes (5-10 cm) through the steam chest at the bottom of the evaporator. This evaporator gives high heat transfer coefficients at high temperature differences, but as the temperature difference reduces heat transfer becomes poor. Liquid circulation past the heating surface is induced by the pumping action of water vapor formed in the tubes. When scaling or salting liquids are to be evaporated it is customary to operate with the liquid level considerably higher than the optimum. To remove scale, the tubes are subjected to cleaning by mechanical devices. The standard vertical tube evaporator is versatile and relatively inexpensive.

SLIDE 8 Thermosiphon Evaporator with External Heater (69-9624)

This type of evaporator gives higher recirculation rates and has a low volume.

SLIDE 9 Forced-Circulation Evaporator (69-9626)

In the forced-circulation evaporator, liquid is recirculated through the heating tubes by a pump at reasonably high velocities with relatively little boiling per pass. Circulation is maintained regardless of the evaporation rate. This type of evaporator is suitable for processing scaling liquids because high liquid velocities in the heating tubes effectively decrease the scale deposition. Present practice tends to install the heating element as a separate unit.

SLIDE 10 Merits and Limitations of Vertical Tube Evaporators (69-9177)(69-9178)

Selection of a forced-circulation evaporator depends upon the economic balance of the construction cost, the cost of energy to circulate the liquid and the improved heat-transfer coefficient obtainable. Another important factor to be considered in radioactive waste treatment is ease of maintenance.

Frequent difficulties: (1) plugging of tube inlets by salt deposits detached from walls of equipment, (2) poor circulation due to higher than expected heat losses, (3) salting due to boiling in tubes, (4) corrosion and erosion.

SLIDE 11 Brookhaven National Laboratory Vapor Compression Evaporator (69-9601)

The highest heat economics in operating evaporators can be achieved by re-use of vaporization energy as a heat source for further evaporation. In vapour compression evaporators the energy potential of low pressure vapour arising from the evaporator is increased by compressing the vapour thereby making the latent heat of condensation available at a higher temperature and resulting in high overall heat efficiency. This type of evaporator has been used at Brookhaven National Laboratory, at Mol in Belgium, Riso in Denmark, and also in France.

Two types of vapour compression are currently used, mechanical compression by a blower and compression by a steam injector.

This slide illustrates the heat balance for the BNL vapor compression evaporator.

Heat Balance

Basis: 1 lb of Distillate

Heat in (Btu/hr)		Heat out (Btu/hr)	
Energy to compressor	25	Net out in distillate	17
Auxiliary steam	57	Venting	12
		Losses	53
Total	82	Total	82

$$\text{Unit efficiency} - 12.2 \quad \frac{\text{lb distillate}}{\text{1000 Btu input energy}}$$

Since about 1,000 Btu are required to vaporize 1 lb of water, this represents a heat efficiency of about 1200% as compared to a single effect evaporator.

SLIDE 12 Merits and Limitations of Vapor Compression Evaporators (69-9179)

AUXILIARY EQUIPMENT

The auxiliary equipment, entrainment separators, condensers, and preheaters are standard equipment types and will not be discussed in detail.

Of these items, the entrainment separators are an important item in obtaining high decontamination factors. The overall decontamination factor is a function of entrainment except where volatile radioactive materials are involved. Therefore, it is necessary to minimize liquid entrainment as far as possible and to remove effectively the entrained liquid drops which are inevitably formed. Simple mist separators which involve a change in direction of the entrained droplets packed columns of wire mesh, and cyclone mist separators are widely used.

Foaming — Foaming is a major problem associated with evaporation of radioactive wastes in many laboratories. Foaming usually occurs when liquids containing colloids, surface-tension depressants or finely divided solids are evaporated and most radioactive waste liquids contain such materials as soaps or detergents in varying concentrations. The presence of air or dissolved gases in the liquid also frequently causes foaming. Once foaming occurs the decontamination factor decreases markedly due to the rise in liquid level, which causes an increase of entrainment and, in the worst case, carry-over of liquid into the distillate. The formation and stability of foam depend upon the kinds and concentration of foaming ingredients in the liquid. At present there is little quantitative information on foaming especially in the field of radioactive waste treatment. The factors which influence foam stability are: surface tension, viscosity, molecular structure of solutes, concentration of solutes and temperature.

When foam increases entrainment it may be destroyed by: foam breakers, liquid-level control, spray jets, mechanical devices such as baffles, chemical anti-foam agents, pH control, acoustic vibrations, and whirling paddles.

Foam breakers collapse foam by using a coiled- or ring-tube installed along the inside wall of the evaporator and located above the top tube sheet. When foaming occurs either steam or cooling water is passed through the tube. Foam breakers may reduce foaming to some extent and most evaporators contain such a device, but they do not suppress foam decisively.

Scaling — The mechanism of scale formation has been studied mainly in relation to boiler or seawater evaporation and very little is known about the formation of scale other than the calcium or magnesium varieties.

a) Addition of small crystal seeds, for example calcium sulfate. The potential deposition of scale on the heating surface is prevented by providing another and more favorable surface on which deposition can occur.

b) Injection of bittern (magnesium sulfate). The addition of bittern increases the sulfate ion concentration in the thick liquor and results in a decrease in solubility of calcium sulfate.

c) Addition of organic materials. The EDTA (ethylene diamine tetra acetic acid) ties up magnesium and calcium ions in a soluble chelate complex.

d) Forced circulation or strong agitation tends to reduce precipitation on the heating surface.

e) Circulation of solid particles such as sand or iron sand through the heating tubes prevents scale formation to some extent, but causes erosion of pump and vessel.

Among these methods forced circulation is the most practicable.

Corrosion – Corrosion is not usually a severe problem in low- or medium-activity liquid evaporation when the feed liquid is neutralized before entering the evaporator. However, when an acidic solution is to be evaporated or when acid is used to remove scale and to decontaminate evaporators, the choise of construction material becomes important. It is common practice to employ stainless steels of A.I.S.I. type 316 or 347. The choise of material should preferably be based on actual testing under operating conditions using the liquids to be processed.

Volatile Nuclides – During evaporation difficulties are often caused by some anions which have a tendency to vaporize, i.e., iodine, ruthenium, tritium, and volatile organic materials. When the solution containing iodine is evaporated under acidic conditions a substantial fraction of the iodine may volatilize. Radioiodine is used frequently in tracer studies and appears in the condensate in the form of iodide. Ruthenium in the form of ruthenium tetroxide is volatile and may reduce the overall decontamination factor. This compound can be formed under strong oxidizing conditions such as in boiling nitric acid and by the presence of ozone or permanganate ions. There is also some evidence that ruthenium distills more readily from dilute acid containing ferric sulfate, sulfuric acid, and sodium nitrate. When tritium is contained in waste in the form of tritiated water, it cannot be removed economically by evaporation but fortunately the concentration of tritium in waste is usually low and can be accepted by the environment since there is no reconcentration effect. As these volatile radionuclides reduce the overall decontamination to ensure through purification of the condensate, treatment by anion-exchange column is effective except for tritiated water and non-eletrolytic organics.

Costs – The cost of evaporation is relatively high. This has been listed by the IAEA panel on the Economics of Radioactive Waste Management where cost analyses from four establishments with chemical treatment and four with evaporation were reported. These cost analyses were prepared for the first time on the same basis. For chemical treatment alone with throughput of 6.3×10^4 to 5.10^5 m^3/yr, the total costs are 0.2 to 1.5\$/m^3, while for evaporation alone with a throughput of 900 to 3.4×10^3 m^3/yr the total costs are 14 to 112\$/m^3.

SLIDE 13 Evaporation Cost as a Function of Capacity (68-12089)

This slide illustrates the very important effect of processing rate on evaporation cost. The amount of shielding required is another important variable.

The ORNL unit includes 5 ft of shielding, is rated at 600 gal/hr, and costs \$40-\$50/1000 gal including amortization over 20 years. About 50% of the \$17/1000 gal cost at Hanford is steam cost (ref. HW-79174).

Because of the large number of variables, one must be extremely careful in quoting and comparing evaporation costs. Many types of cost comparisons are given in the IAEA Technical Report # 87 on evaporation.

REFERENCES AND EXCERPTS FROM:

1. *Design and Operation of Evaporators for Radioactive Wastes,* Technical Reports Series Nº 87, IAEA, Vienna, 1968.

2. E. Malasek, "Operation of Evaporators for Liquid Radioactive Wastes," IAEA Regional Training Course on Radioactive Waste Management, Rio de Janeiro, Brazil, October 14-25, 1968.

3. B. Manowitz, "Engineering Results on the BNL Semi-works Vapor Filtration Compression Evaporator, *"Progress Report on Waste Concentration Studies, V.* BNL-121 (T-24), August 15, 1951.

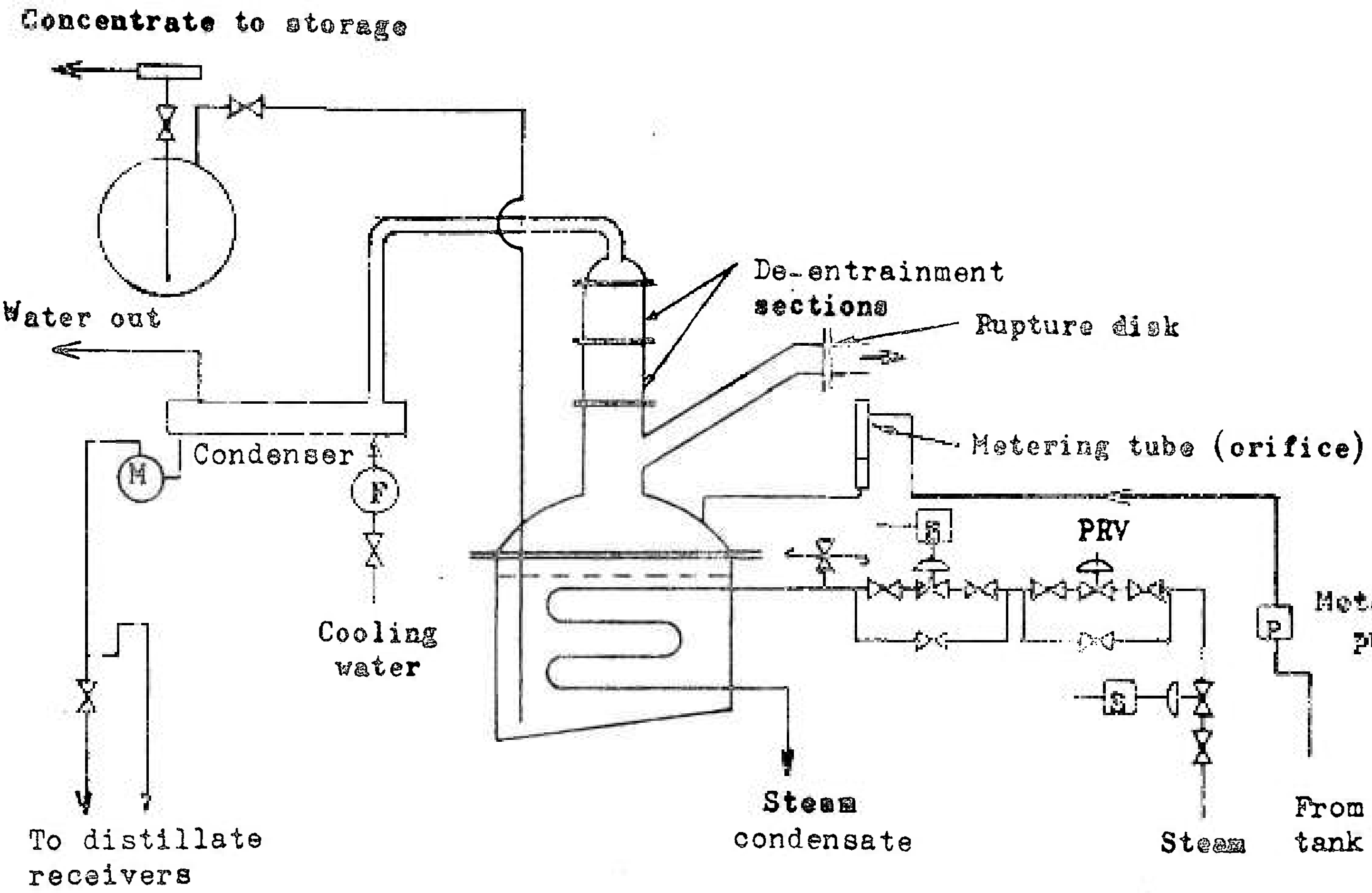
4. F. N. Browder, "An Evaporator for Intermediate-Level Radioactive Waste at Oak Ridge National Laboratory,".

FACTORS IN CHOICE OF EVAPORATOR TYPE

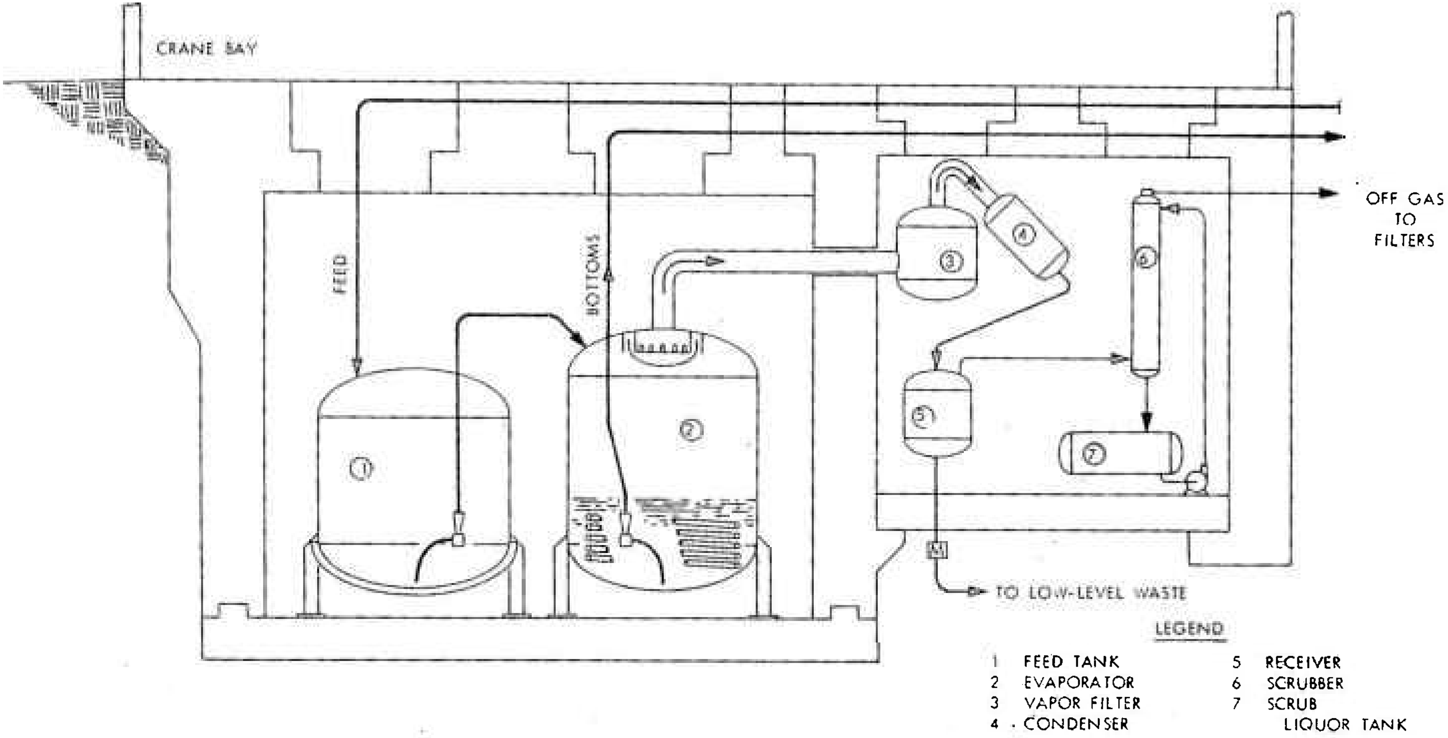
1) Feed characteristics: type and concentration of salts and radionuclides, salting, scaling, corroding, and foaming
2) Processing rate, fluctuation, working hours per day
3) Decontamination factor required
4) Ease of maintenance
5) Space and (shielding) limitation
6) Economic limitations

EVAPORATOR TYPES

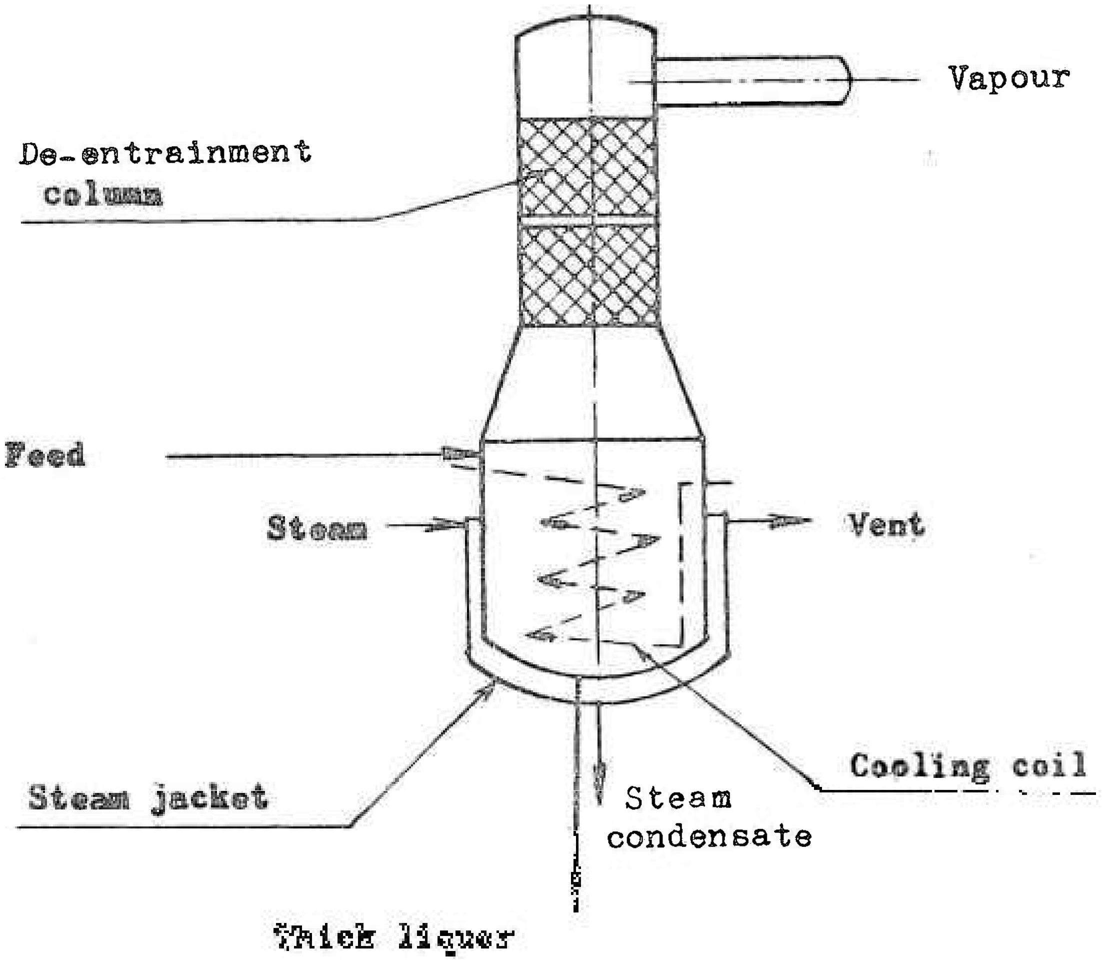
COMMONLY USED	LITTLE USED
Coil	Horizontal tube
Pot or jacket	Multiple effect
Vertical tube (natural)	Wiped film
Thermosiphon (external tubes)	Falling film
Forced (external tubes)	Rising film
Vapor compression	Flash
	Spray dryer
	Submerged combustion



CHALK RIVER COIL EVAPORATOR



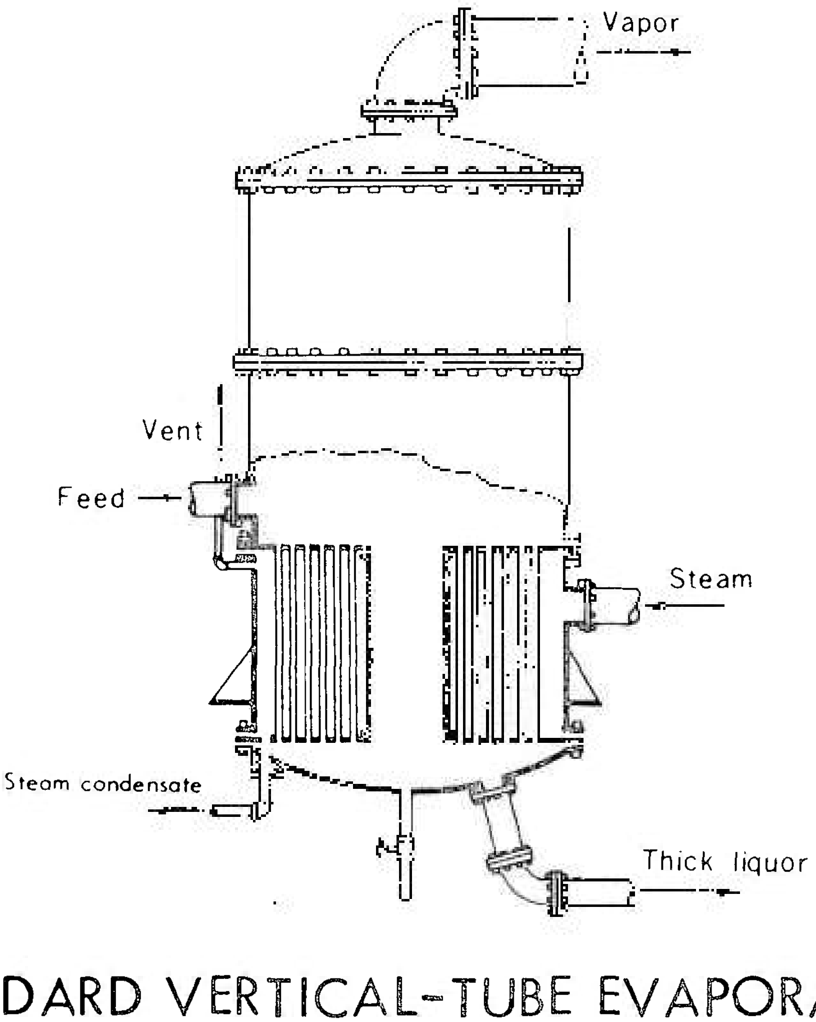
ORNL INTERMEDIATE-LEVEL WASTE EVAPORATOR



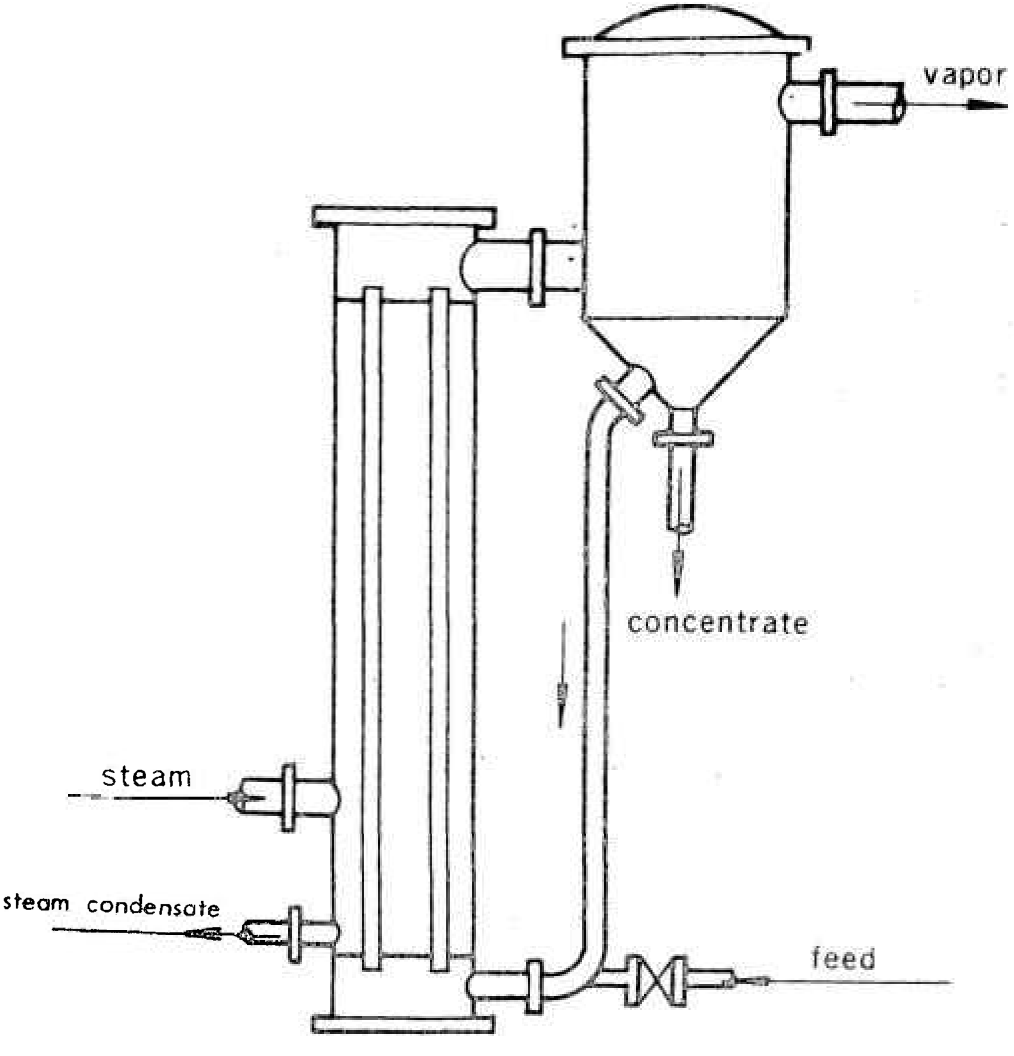
STEAM-JACKETED KETTLE

MERITS AND LIMITATIONS OF COIL AND JACKET EVAPORATORS

TYPE AND LOCATION	MERITS	LIMITATIONS
Coil (ORNL) (Chalk River) (Harwell)	1. Simple construction 2. Suitable for scaling liquids (designed for coil replacement) 3. Easy maintenance 4. Low cost 5. High volume reduction	1. Small heating surface per evaporator volume
Jacket (Small installations)	1. Simple construction 2. Easy maintenance 3. Low cost 4. High volume reduction	1. Small heating surface per evaporator volume

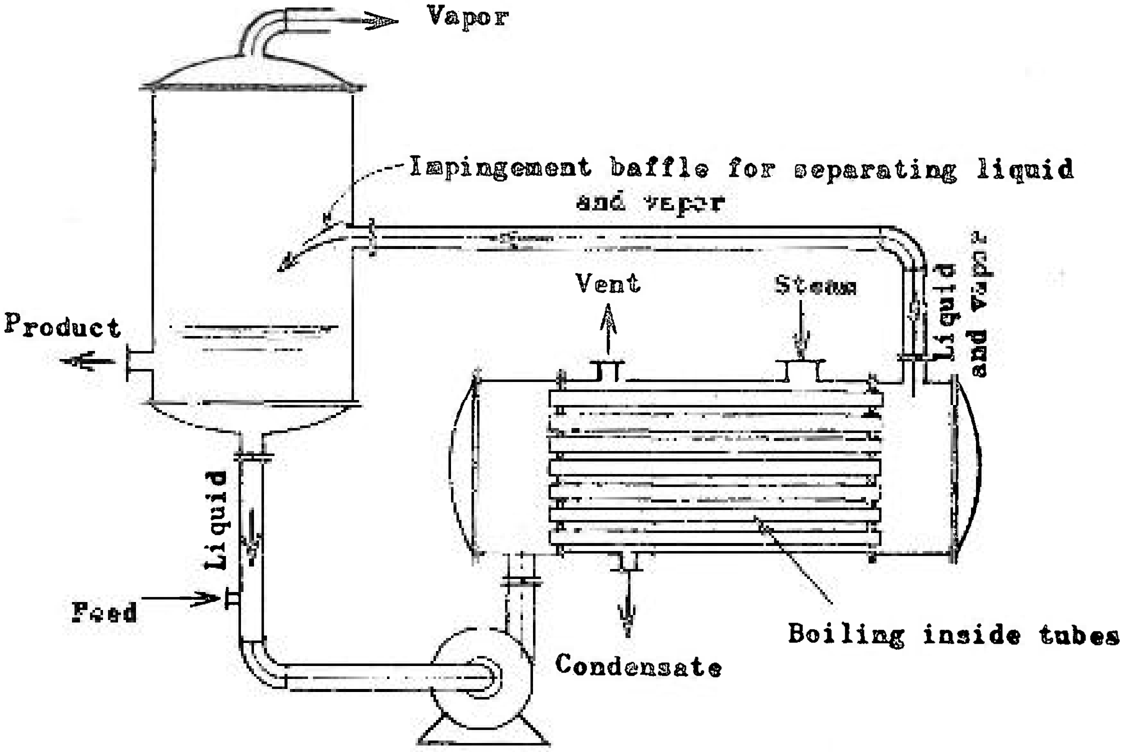


STANDARD VERTICAL-TUBE EVAPORATOR



EVAPORATOR WITH EXTERNAL HEATER

(thermosiphon)



FORCED-CIRCULATION EVAPORATOR

MERITS AND LIMITATIONS OF VERTICAL TUBE EVAPORATORS

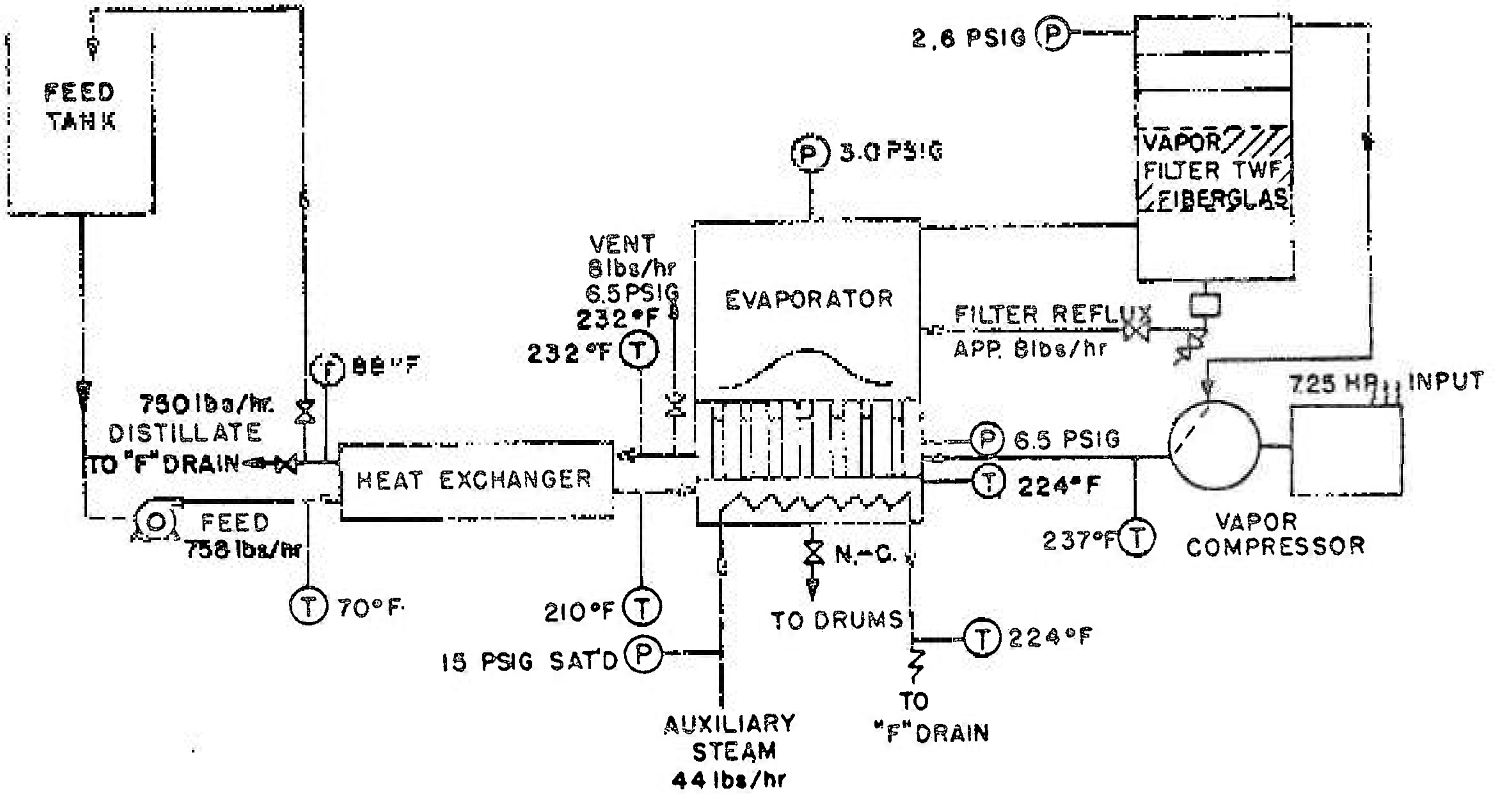
TYPE AND LOCATION	MERITS	LIMITATIONS
Standard-vertical tube-natural circulation (Hanford, Savannah River)	1. High heat transfer coefficient 2. Less expensive 3. Suitable for all liquids including high-level waste 4. Easy maintenance (tube replacement	1. Some difficulty in mechanical removal of scale
Thermosiphon-vertical external heater-natural circulation (Idaho)	5. Higher heat transfer coefficient 6. Potentially lower evaporator volume	

ORNL DWG. 69-9178

Part 2

MERITS AND LIMITATIONS OF VERTICAL TUBE EVAPORATORS

TYPE AND LOCATION	MERITS	LIMITATIONS
Vertical tube (forced circulation) (Saclay, Marcoule)	1. Suitable for scaling liquids 2. High heat transfer coefficient (higher than natural circulation types) 3. Easy maintenance (tube cleaning of heating tubes for vertical-tube type)	1. High cost 2. Possibility of plugging of tube inlets 3. Unsuitable for liquids containing corrosive or erosive materials

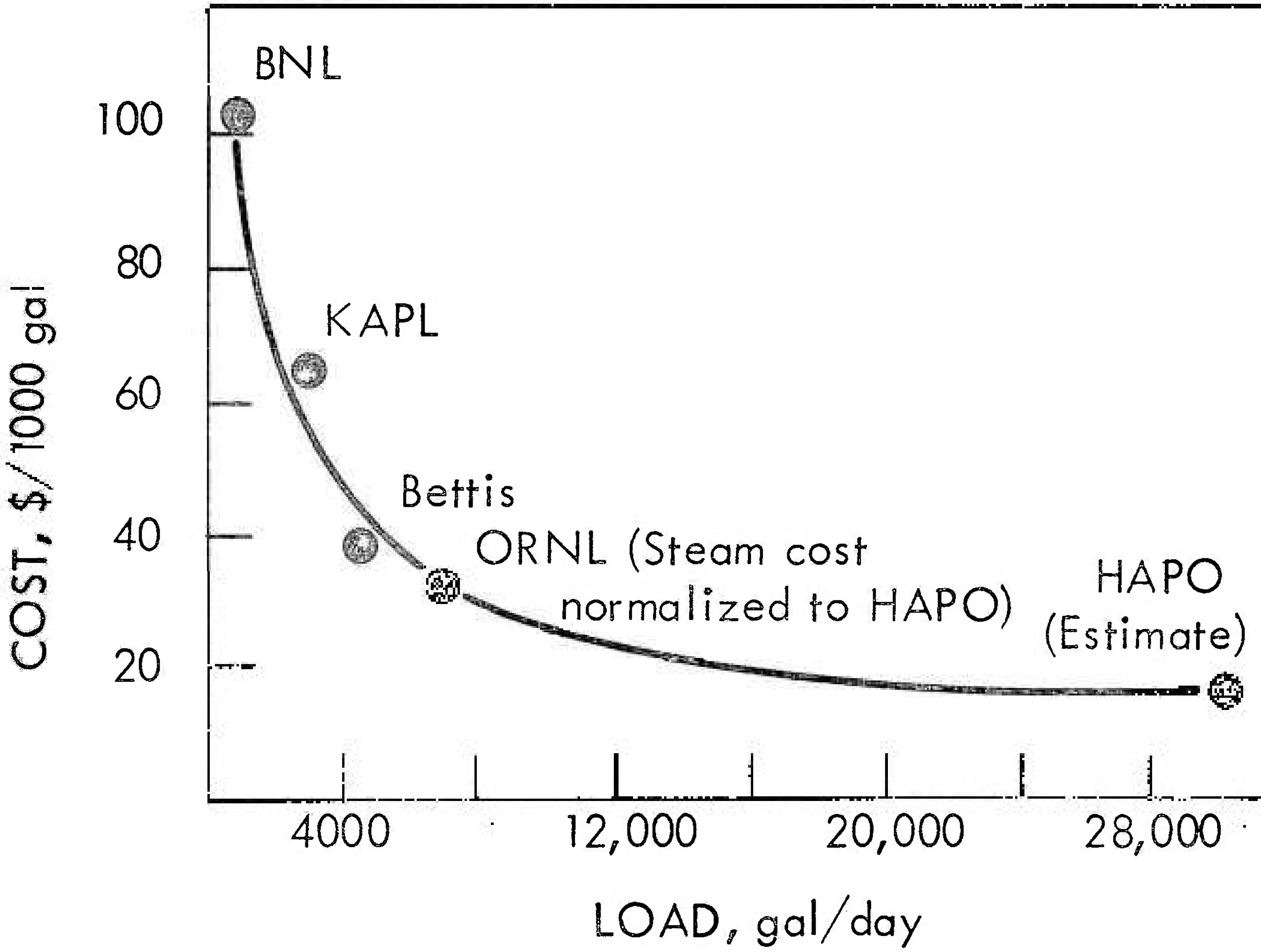


BROOKHAVEN NATIONAL LABORATORY VAPOR COMPRESSION EVAPORATOR

ORNL DWG. 69-9179

MERITS AND LIMITATIONS OF VAPOR COMPRESSION EVAPORATORS

TYPE AND LOCATION	MERITS	LIMITATIONS
Vapor compression (Mol, BNL, RISØ, Grenoble)	1. High heat economics for relatively large capacity	1. Necessity for larger heating surface 2. Uneconomical for evaporation under reduced pressure 3. Limited range of optimum steam pressure for steam injector type 4. Uneconomical for small capacity


BNL
KAPL
Bettis
ORNL (Steam cost normalized to HAPO)
HAPO (Estimate)
100
80
60
40
20
COST, $/1000 gal
4000
12,000
20,000
28,000
LOAD, gal/day

TREATMENT OF LOW- AND INTERMEDIATE-LEVEL WASTE CONCENTRATES

R. E. Blanco

INTRODUCTION

In previous lectures we discussed methods for treatment of low- and intermediate-level radioactive wastes to produce purified water for discharge and concentrates containing the radionuclides. In this lecture we will discuss methods for handling the concentrates and, in a future lecture, methods for disposal of the final waste solids.

All treatment processes for the handling of low- and intermediate-level wastes produce a concentrate which, generally, has to be conditioned before final disposal. These concentrates may be the sludge from evaporation plants, chemical treatment sludges, or spent ion exchange material. Methods in use include solar evaporation, filtration (gravity, pressure, drum), centrifugation, and incorporation into asphalt (called bitumen in Europe) or into cement or cement-vermiculite.

SOLAR EVAPORATION AND FILTRATION

SLIDE 1 Solar Evaporation Plant at Lucas Heights, Australia (Photo 97014)

At Lucas Heights, near Sydney, Australia, where solar evaporation is practiced, sludge originates from a low-level effluent treatment plant in which a scavenging-flocculation process, using aluminum hydroxide precipitation, is operated. The sludge produced consists mainly of aluminum hydroxide and occasionally contains small amounts of surfactants and solvents. The plant consists of a concrete pond, 86 m^2, divided into four compartments. It is surrounded by a kerb, 30 cm high, and has a usable volume of 23 m^3. It is fitted with a flat, steel, movable roof on rails mounted on the kerb. The roof has hinged side panels so that the sludge surface can be exposed to controlled air movement when it is in position. The roof can readily be moved by one man. The pond was built for another purpose and the design as an evaporator is therefore not fully utilized. The pond is filled with 10 cm of sludge. When the sludge has reached the consistency of a stiff paste it is cut into squares (7.5 cm x 7.5 cm) by drawing through it a simple long-handled multi-bladed knife. This process has two effects: first, it increases the area from which evaporation can occur; and secondly, it reduced the spalling and consequently the amount of fines produced when the dried sludge is handled and thus the amount which becomes airborne. When, in 30 to 40 days, the sludge cake has reached a moisture content in the range of 23-33%, it is removed from the pond by shovelling into drums.

Respiratory protection for personnel performing this operation has been found to be unnecessary, as air and surface contamination levels have been found to be well below the Recommendations of the International Commission on Radiological Protection and Research Establishment health and safety levels. About 114 m^3 of sludge is produced each year. The waste is reduced in volume by a factor of 20 from waste to final product. The latter contains about 25% water.

SLIDE 2 Natural Filtration on Beds, Harwell (Photo 97020)

This slide shows the gravity filtration method used at AERE, Harwell, United Kingdom, for the concentration of sludges resulting from the treatment of low-level active effluent ($< 10^{-4}$ Ci/m^3). The sludge consists mainly of calcium phosphate, with a small amount of ferric hydroxide. The use of processes designed to de-water chemical sludges by simple gravity filtration on beds of sand or anthracite has not been extensive although some sludges are amenable to this type of treatment. Clogging of filter media, very low rates of filtration and low volume reduction have been experienced at some of those facilities where studies or operations have been carried out. The total amount of sludge treated during 1965 was 1400 m^3, but of course the method can easily be used for much smaller volumes by using fewer and smaller beds. After treatment the sludge is dug off the beds and placed in unshielded mild steel drums. The drums contain 160 liters of sludge plus 20 liters of ballast to give a density greater than 1.2 and so be suitable for sea disposal.

The sludge is pumped onto the filter bed using a positive displacement pump ("MONO" 23 m^3/hr rating). The beds are of brick construction, 10.2 m x 4.3 m x 1.1 m high, with a filter bed consisting of land drains in a 81-cm thick layer of graded gravel with a surface layer of 10-cm sand. They are covered by a simple structure to avoid troubles during rainy weather.

Treatment is in batches of up to 30 m^3 and filtration times normally vary between one and three weeks according to ambient conditions. (If winter, and the sludge freezes, it is impossible to dig it off until it has thawed.) Filtrate from the bed flows out into a sump and is pumped back to the untreated effluent system.

After filtration the sludge is shovelled into unshielded mild steel drums. These stand on a roller conveyor situated alongside the beds and can easily be moved along manually to the storage area when filled. During the digging operations the men wear protective clothing to guard against contamination, and health physics personnel are in attendance to measure radiation levels and air contamination.

The volume reduction achieved, between sludge going onto the bed and that in the ballasted drum, is 4. The solids content before treatment is 3% to 3.5% and after, 12% to 15%.

This system has been in operation for eleven years and has given very little trouble. Operation is very simple and maintanance almost negligible. The only labor requirement is removal of sludge from the beds. The disadvantages of the process are the low concentration factor achieved and the fact that, owing to radiation and contamination dangers, only low-level sludges can be treated.

SLIDE 3 Diagram of "Sweetland" Filter Circuit, Harwell (69-10070)

This slide shows the pressure filter system used at Harwell, United Kingdom (also in Hahn-Meitner Institute, West Germany). Two types of sludge are treated, one consisting of calcium phosphate and ferric hydroxide and the other of calcium phosphate and copper ferrocyanide with a small amount of ferric hydroxide. They contain about 0.5 Ci/m^3 beta-gamma activity, mainly aged mixed fission products, and a small amount of alpha activity, chiefly uranium and plutonium. The plant can filter raw sludge at a rate of 360 m^3/yr per 8-hour day. After concentration, the sludge is packed into 90-liter capacity mild steel drums. These are located in larger steel units which provide 5 cm of concrete shielding between the steel layers. The overall volume for sea disposal is 180 liters. The filter consists of a series of circular filter leaves suspended inside a cylindrical cast-iron shell with the flat faces of the leaves perpendicular to the axis of the cylinder. The shell is divided along the horizontal center into two halves hinged together along the back. The upper half is rigidly fixed to supports so that the lower half can swing open, thus exposing the interior of the filter for emptying and cleaning. The edges of the two halves of the cast-iron shell hold a gasket which forms a tight joint when the filter is closed. Nylon bags are placed over the filter leaves.

Sludge is supplied to the filter under pressure. The liquor is forced through the nylon cloth and issues from the individual outlets through sight glasses. The solids are stopped by the cloth and collect on both sides of each leaf in the form of a cake. When the pressure builds up to 2.45 kg/cm^2, the feed is shut off and the excess wet sludge is expelled by compressed air at a sufficient pressure to hold the cake in place. The air flow is continued after the wet sludge is evacuated to effect some drying of the cake. Air direction is then reversed and the sludge cake is blown from the leaves into the bottom of the vessel. The press is finally opened and the concentrated sludge falls down a chute into a disposal drum.

The volume reduction achieved between sludge fed to the filter and that in the disposal drum is about 12. If the final waste has to be shielded with 5-cm concrete, as is usually necessary, the volume reduction factor is reduced to 6. The solid content of the untreated sludge is 1,5% to 3% and that of the final waste 20 to 22%.

This plant has been in operation for over 16 years. It is fairly simple to operate and needs little maintenance. Filter leaves are cleaned regularly and the cloth replaced periodically. This disadvantages of the system are the comparatively low concentration factor and the possibility of air contamination.

SLIDE 4 "Sweetland" Pressure Filter, Harwell (Photo 97022)

SLIDE 5 Vacuum Filter, Los Alamos (Photo 97019)

Vacuum filtration is a common method for concentrating sludges. Precoat-type vacuum filters using diatomaceous earth for the filtering medium have been found to be effective for most sludges. In certains cases pretreatment of sludge by the freeze-thaw step, which will be discussed later, or by polyelectrolytes, will substantially improve filtration rates and volume reductions.

Three modern vacuum filtration plants, one located in France, one in the United States, and one in India, are discussed. All of these plants treat chemical sludges from co-precipitation processes.

This slide shows the vacuum filter used at Los Alamos, USA, for concentrating sludges of ferric hydroxide-calcium carbonate.

SLIDE 6 Vacuum Filter, Precoated with Diatomaceous Earth, Los Alamos (Photo 97021)

This is the interior of the Los Alamos vacuum filter.

The knife blade moves forward into the precoat at an average rate of about 0.5 cm per hour and cuts of the sludge plus a small amount of filter aid. The sludge-filter aid falls onto a screw conveyor and is ultimately deposited into a 200-liter steel drum. At this point the de-watered sludge contains about 40% to 50% solids. The drum is sealed, monitored, and loaded into a conveyance for transfer about 3 km distant to a solid-waste burial pit for final disposal.

This type sludge treatment has been practiced at Los Alamos since 1950. In the first few years the filter operation time was, by present standards, excessive. In 1955 the addition of a coagulant aid, Separan, to the coagulating chemicals was initiated. The Separan not only improved coagulation efficiency but also affected the sludge beneficially in that higher filtration rates and higher solids concentration in the final product were obtainable. More recently the control of zeta potential by the addition of cationic polyelectrolyte to the coagulating chemicals has been initiated at LASL. A further improvement in the filtration rate was noted.

In a typical month 4220 m^3 of waste produces 38 m^3 of wet sludge, which results in 5.4 m^3 of filter cake. This is at a filtration rate of 150 liters of wet sludge per m^2/hr resulting in 21 liters filter cake per m^2/hr.

SLIDE 7 Rotary Vacuum Filter, Effluent Treatment Station, Marcoule (Photo 97023)

This shows the vacuum filter used at Marcoule, France. The sludges resulting from the treatment of medium high-activity waste are of the colloidal type, and the solid material contained in them has the following average composition:

$Fe(OH)_2 + Fe(OH)_3$	:	35%
$Ni_2Fe(CN)_6$	:	35%
Diatomaceous earth	:	30%

After vacuum filtration the colloidal type sludges contain a much lower percentage of solids than the crystalline sludges in which the main constituent is calcium carbonate. The colloidal sludges have 18% to 22% solid material together with a correspondingly high water content and a density of 1.12 to 1.15. The high water content is eliminated at a reasonable cost by means of the coating process, a bitumen encasing technique developed in Marcoule. The coating process eliminates the need for prefiltration sludge conditioning procedures. The technique is discussed in detail later.

After almost ten years of operating experience it can be concluded for the following reasons that vacuum filtration is a reliable method for concentrating sludges:

a) The equipment is sturdy and well-built;

b) Breakdowns are rare; and

c) Decontamination is simple.

At this particular plant because of the high specific radioactivity levels it is necessary to:

a) Protect operating personnel against radiation;

b) Incorporate remote controls into the system;

c) Ensure adequate ventilation;

d) Prevent the spread of contamination;

e) Clean the vessels and pipes with decontaminating solution; and

f) Provide for rapid dismantling of the pumps.

SLIDE 8 Freeze-thaw Vacuum Filtration Unit, Mol (69-10071)

This slide shows the freeze-thaw plus vacuum filtration process used at Mol, Belgium since 1960. All sludges coming from very low- and intermediate-level radioactive effluents are treated in this manner. The freeze-thaw technique concentrates the solids and more water is removed during filtration. Due to the origin and composition of the waste to very low activity effluents, which are treated by aluminum hydroxide flocculation, produce a sludge containing relatively large amounts of organic material — about 20% of the total solids. The low- and intermediate-level radioactive effluents are treated by a combined precipitation-flocculation system which generates precipitates of $BaSO_4$, $Cu_2Fe(CN)_6$, $Fe(OH)_3$ and $Ca_3(PO_4)_2$. Initially, the combined sludge was filtered after the freeze-thaw step by centrifugation in a horizontal-drum centrifuge. However, since 1964 the centrifuge has been replaced by a small rotating drum filter which feeds the filtered sludge into the bitumen-insolubilization plant.

The sludge resulting from gravity settlement and containing less than 4% solids is pumped into the freezing tanks, which are provided with external double-wall cooling together with internal cooling plates. The complete freeze-thaw cycle takes about 5-1/2 hours. After thawing, a thick slurry settles to the bottom of the freezing tanks. The clear supernatant is removed and recycled into the chemical treatment system. The slurry, which contains about 15% solids, is then pumped to the filter. The second pumping stage is necessary for regular and continuous feed of the rotating drum unit.

The quantity of sludge which is treated per year is approximately 750 m^3, of which about 275 m^3 result from the treatment of very low activity effluent.

SLIDE 9 Volume Reduction During Successive Steps of Treatment at Mol (69-9259)

INCORPORATION IN CEMENT

Incorporation in cement is the common method for solidifying and making wastes insoluble before storage or burial. Almost all countries use it to some extent. The purpose of the treatment is to fix and prevent the re-dispersal of radioactive nuclides upon disposal by burial, sea disposal or storage methods. As a secondary benefit, the cement acts as a radiation shield of particular value for those situations where sludge radiation levels are high.

For low-level sludges, incorporation into cement is adequate treatment, especially if the solidified blocks are to be stored or buried in containers from which rain and ground-water are excluded. It is adequate treatment for intermediate-level sludges when the radionuclides of concern are ^{89}Sr and ^{90}Sr, ^{239}Pu or ^{241}Am, since these nuclides are tightly bound. However, when cesium or ruthenium are involved, leach rates from the intermediate-level sludge-cement mixtures will be relatively high and additional protection may be required. The addition of illitic clay to the cement mixture has been found to improve retention of the Cs and Sr. Fixation in cement is practiced for the insolubilization of chemical sludges, concentrates resulting from evaporation, spent ion-exchange materials and certain high-activity waste solutions.

Many types of mixing units have been studied and are described in the literature.

SLIDE 10 Drum Used for Final Disposal, Los Alamos (69-10067)

This slide shows a simple system at Los Alamos, USA, where the cement and waste are mixed in the final disposal drum. Similar mixing is carried out at Fontenay-aux-Roses, France, and many other installations.

A 60-liter drum containing a maximum of 120 kg of cement and two brick halves to facilitate mixing is so located inside a 200-liter drum that 114-cm mortar shielding is provided in the annular space and 12.7 cm of mortar shielding is provided at top and bottom. The filling and vacuum pipes are capped after the transfer of the neutralized solution to the 60-liter container, then drum is placed in the tumbler and the contents are mixed for 15 min. This procedure fixes the radioactivity in the mortar and the shielding prevents excessive exposure to operating personnel. To protect personnel further, regulations stipulate that the radioactivity is to be less than 200 mR at one meter from the drum for unescorted carriers. This requirement determines the amount of solution that is treated in each batch.

SLIDE 11 Flowsheet for Incorporation of Wastes in Cement, Los Alamos (69-10065)

This slide shows a new system at Los Alamos that uses a pug mill for continuous cementing of wastes. The wastes are:

a) A solution containing approximately 1 mg/liter each of ^{239}Pu and ^{241}Am and 25 to 35% solids, mostly sodium nitrate.

b) Ferric hydroxide sludge resulting from chemical treatment of low-level wastes.

c) Miscellaneous alkaline batch wastes.

Waste from the storage tank is pumped through a magnetic flow meter into the center of the front end of the pug mill at a rate of about 45 liter per minute. Cement from the storage silo is fed to the same area of the pug mill by a screw conveyor at a rate of about 65 kilograms per minute.

The pug mill is equipped with two shafts with attached paddles, 13 cm x 13 cm which rotate in opposite directions at a speed of 72 rpm. The paddles are slanted so as to move the mixture towards the back end of the mill as the cement and wastes are mixed. They also have scrapers attached which keep the rubber-lined chamber clean so that no cement will remain to harden and present later problems. At the back end of the mill the slurry falls into an open throated Mayno pump and is pumped through an underground 6.3-cm pipe to pits in the disposal area 50 meters distant. The disposal pits are wells 2.5 meters in diameter and 20 meters deep.

Samples of the slurry are collected at regular intervals for determination of compressive strength and leach rates.

To prevent airborne contamination the pug mill is equipped with a removable lucite cover, and the air pressure inside the mill is maintained at slight less than atmospheric by exhausting air through an absolute filter with a blower. Air samples are taken in the immediate mill area and throughout the building to detect any airborne contamination. To date no excessive concentration of radioactivity has been detected.

Adjacent to each disposal well is a 5-cm-diameter test hole used to detect any movement of radioactivity or water. No water or radioactivity has been detected leaving wells containing the cement slurry.

SLIDE 12 Pug Mill for Incorporating Wastes in Cement, Los Alamos (Photo 97016)

SLIDE 13 Interior of Pug Mill for Incorporating Wastes in Cement, Los Alamos (Photo 97017)

Similarly, other installations pump cement into underground permanent monoliths. In the USSR the cement mixture is poured into underground concrete tanks of 600 m^3 capacity where it solidifies and remains in place. The system is straight-forward and inexpensive and contamination problems are reported to be very small.

At Brookhaven National Laboratory in the United States, evaporator concentrates were formerly mixed with cement in a batch-type mixer and poured into the 200-liter drums to harden. The use of these small drums became impractical in 1959 when the quantity of waste and associated external radiation levels increased. Reinforced concrete vaults (normally 1.5 x 1.5 x 1.9 m) that may weigh up 10 tons when filled are now used. Wall thickness is normally 15 cm, but may be increased to 43 cm for special gamma shielding. Waste slurry from the evaporator is solidified in the 15-cm wall concrete vaults by the addition of exfoliated vermiculite (2.7 m^3 per vault) and Portland cement (0.68 m^3 per vault). Vermiculite is used for its absorptive capacity, and the cement provides the necessary strength. The mixture will expand less than cement alone, thus eliminating hairline cracks in the vaults. An external batch mixer was used initially but experience has shown that adequate mixing of slurry with vermiculite and cement is obtained by introducing the slurry into the partially filled vault through a perforated pipe.

INCORPORATION IN ASPHALT

Incorporation in asphalt has two important advantages over incorporating in cement; i.e., (1) the product can contain high (50-60 wt %) concentrations of solids and (2) the water is eliminated by evaporation. Cement becomes weak if it contains over a few percent of soluble salts. Cement also retains all of the water in a waste concentrate, thus preventing a large volume reduction. Both products have low leach rates in water. Asphalt has the disadvantage that it could burn if ignited in an above ground storage area fire. After burial, this disadvantage is eliminated.

SLIDE 14 Insolubilization in Bitumen, Mol (69-10069)

This slide shows the asphalt process used at Mol, Belgium. The processes at Harwell, United Kingdom, and Karlsruhe, West Germany, are very similar. The radioactive concentrate, which is in the form of a liquid slurry or filtered solid of high moisture content, is introduced under vigorous mixing into a liquid bitumen bath, temperature of which is maintained at 150°C or 230°C, depending upon the type of bitumen. During the mixing process the water is completely evaporated and the solid residue is uniformly dispersed into the bitumen. When a concentrate of 40% to 45% of dry solids in the bitumen is reached, injection of concentrate is stopped and the liquid mixture is transferred into disposal drums. The off-gases contain water vapor and contaminated particles and require treatment by washing or condensation and electrostatic precipitation.

In April, 1964 a full-scale plant with an evaporator capacity of 100 liters of water per hour was started. The majority of concentrate handled in the plant results from freeze-thaw-vacuum filtration and contains primarily $Al(OH)_3$, $Fe(OH)_3$, $Cu_2Fe(CN)_6$, $Ca_3(PO_4)_2$, $BaSO_4$ and 60 to 65% of water. The average activity level of the output product has varied from 1 to 10 μCi/ml.

Due to the very low leaching rate of the bitumen mixture, it is believed that the output material can be disposed of safety on land despite the very unfavorable site conditions prevailing at Mol. The United Kingdom, France, and Belgium apparently also consider sea disposal as practical and desirable.

Mexphalte 10/20 was recently replaced by the bitumen Shell PH-55-65 which allows operation at 160°C. Although this type of bitumen has been used for only a short term, it appears to offer the same characteristics of hardness of the final product. It provides the advantage, however, of decreased entrainment with the off-gases.

There is strong evidence that entrainment with off-gases and the formation of aerosols will be very much reduced by using lower melting bitumen. In a long series of tests with Shell PH-55-65 at 160°C it was shown that entrainment of bitumen with the water vapor varied between 0.015% and 0.060% of the amount of water vapor. Condensation and electrostatic filtration of the off-gases further reduces their bitumen and oil content to a value where absolute filters are applicable.

SLIDE 15 Installation for Insolubilization of Ash and Vermiculite, Mol (69-10066)

This slide shows the installation for direct incorporation of ashes or sands in asphalt.

SLIDE 16 Bitumen Coating Machine, Marcoule (Photo 97018)

This slide shows the machine used to coat the solids sludge particles with asphalt (bitumen). The first, or pre-coating, stage of the bitumen coating process for treating sludges from the co-precipitation plant is the elimination of most (85 – 90%) of the constituent water. This is accomplished by deliberately creating an unstable bitumen-sludge emulsion using suitable surface-active agents. The emulsion breaks down almost immediately (after 15 to 20 s), and the solid particles of the sludge are coated by the bitumen while the constituent water is eliminated. At this stage most of the radionuclides adsorbed on the sludge are immobilized. However, the resulting coated material still contains some water (7% to 10%) and the mineral particles are not perfectly dispersed in the bitumen.

In the second stage the intimate mixing of the mineral particles with the bitumen is continued and the water in the coated material is completely evaporated. The mixing temperature is raised to 140°C to 150°C, reducing the viscosity of the final product and permitting complete homogenization and gravity flow. The time required for complete dehydration is about two minutes.

The bitumen chosen for coating sludges at the effluent treatment station is a Shell bitumen produced by direct distillation. For medium-activity sludges having calcium carbonate as their main constituent, Mexphalte 40/50 was selected.

In coating medium-activity sludges, 45 to 50 parts of Mexphalte are used per 100 parts of dry sludge. The final coated material after dehydration (water content less than 0.5%) thus contains 31% to 33% bitumen. For high-activity sludges having ferrous hydroxides and nickel ferrocyanide as their main constituents, Mexphalte 80/100 was selected and 150 parts are used for 100 parts of dry sludge. The final coated material after dehydration (water content less than 1.5%) thus contains 60% bitumen.

SLIDE 17 Various Details of Coating Machine, Marcoule (Photo 97015)

The coating machine was developed from a conventional plastic extruder with two screws turning in the same direction. Its originality lies in the design of the screws, the presence of the mechanism for extracting the water released from the coated material, and the location of the mechanized drive outside the hot zone.

The coating machine consists of four sections, the first of which provides thorough mixing for the cold sludge, the surface-active agent and the hot bitumen. These are fed by gravity into a chute from which they are picked up by transport screws and forced into the horizontal body of the machine. The coating of the material and the separation of the water are carried out in the second section, as the material passes through the body of the machine. This section consists of a succession of triangular kneading elements and transport elements.

Water is released and the coated material is removed in the third section. A mixture of coated material and water enters, passing through successively low- and high-pressure zones.

There are two outlets blocked by a pair of screws which turn in the same direction. The pitch and speed of rotation of these screws are such that the viscous-coated material is forced back and held in the body of the machine while the water flows out along the threads of the screws.

In the fourth section the material is heated to 105°C to 110°C as it passes through and is then fed to the dehydration machine. Temperature control is critical.

SLIDE 18 Automatic Revolving Turntable, Marcoule (Photo 97024)

The product flows into drums at 140-150°C. Advantages of this process include:

a) Low amounts of heat required since water is not evaporated.

b) Tars and heavy oils are not volatilized or entrained at the low temperatures used and the low mixing rates.

Disadvantages include:

a) Close operating control to maintain a homogeneous feed to the mixer.

b) Soluble radionuclides, such as $^{137}CsNO_3$, will remain in the water unless they are made insoluble by the use of expensive reagents such as ferrocyanide.

SLIDE 19 Waste Residues Which have been Incorporated in Asphalt and/or Polyethylene (69-7224)

This slide shows the various types of wastes which have been incorporated in asphalt at various nuclear installations.

SLIDE 20 Flowsheet for Asphalt Process (65-659 R1)

This slide shows the schematic flowsheet for the asphalt process developed at Oak Ridge National Laboratory. The asphalt (or polyethylene) incorporation procedure generally involves (a) mixing the waste solution, slurry, or solids with commercial emulsified road asphalt (35 wt % water) or molten-base asphalt (or molten polyethylene) at a temperature where the matrix is fluid (approximately 25 to 160°C) and (b) increasing the temperature to approximately 160°C to evaporate the waste fluid. The solids remain intimately dispersed in the asphalt (or polyethylene) which flows out the bottom of the evaporator into a receiver vessel. Emulsified asphalt has been used extensively in the process developed at ORNL because it flows readily at room temperature and is easily pumped. Attractive features of the process include use of emulsified asphalt, which flows readily at room temperature; evaporation at low temperatures to minimize degradation of the asphalt; relatively low agitation rates, which provide adequate mixing and keep the heated surfaces of the evaporator clean; operation in either a batch or a continuous manner; general applicability to all waste types; and retention of both soluble or insoluble solids solids with equal effectiveness. While retention of nonradioactive soluble salts is desirable to prevent their discharge to the environment, the retention of oxidants, such as nitrates, does produce significant operational and safety problems. Most low and intermediate-level aqueous radioactive wastes contain high concentrations of sodium nitrate and the safety aspects of producing and storing an asphalt product containing high concentrations of nitrate must be carefully assessed. Thus, the development program at ORNL has been directed almost exclusively to processing the major waste types, which contain nitrate, and assessing the safety problem. Other waste types, which do not contain nitrate, can undoubtedly be processed by the same method. The incorporation of organic wastes has been studied intensively at ORNL. Organic materials with boiling points higher than approximately 160°C remain in the asphalt or polyethylene product. Polyethylene has proved to be superior to asphalt for all organic wastes, particularly in instances where high concentrations of organic materials are desired in the residue. Chlorinated hydrocarbons and other hydrocarbons have also been dispersed in polyethylene. For example, about 40 wt % tributyl phosphate (TBP) has been incorporated in polyethylene to yield a satisfactorily hard product. Asphalt products containing as much as 25 wt % TBP, on the other hand, are soft, and up to 37 wt % inert Attapulgite clay powder must be added as a stiffening agent. However, asphalt products containing less than 25 wt % organic materials are harder at room temperature, and stiffening agents are not required.

SLIDE 21 Schematic Flowsheet ORNL Asphalt-Waste Salts (66-178R)

This slide shows the engineering flowsheet for the ORNL asphalt process. Two volumes of waste plus one of asphalt makes two volumes of product.

SLIDE 22 Cutaway Drawing of Wiped Film Evaporator (66-180)

The waste and asphalt are mixed continuously and flow down the side of the Pfaudler evaporator where the rotating blades squeeze the mixture on the sides. The blades rotate at 285 rpm. A 4 ft^2 unit will process 8 to 11 gal of waste/hr. A variety of units for either batch or continuous installations are available commercially.

SLIDE 23 Wiped-Film Evaporator as Installed for Development of the Waste-Asphalt Process (Photo 84202A)

SLIDE 24 Compositions of Simulated ORNL Intermediate-Level Waste (ILW) Solution and an Alphalt-Product Incorporating Solids from ILW (65-12137)

Intermediate level waste contains high concentrations of salts and approximately 1 mCi to 1 Ci/liter of radioactivity. This slide shows a typical waste derived from ORNL evaporator bottoms. If this waste is mixed with emulsified asphalt and the water removed with emulsified asphalt and the water removed by distillation, the product shown in the second column is produced. Both soluble and insoluble solids are retained in the asphalt.

SLIDE 25 Leach Units (69-9258)

This slide shows some of the leach units that have been used to describe the rate at which activity is removed from waste solids. The numerical value of the first and second unit are the same, but the terminology of the second unit, fraction leached $(cm^2/g)^{-1}$ day^{-1}, appears superior since it avoids the easily misinterpreted term, g cm^{-2} day^{-1}. Dividing these leach units by the product density expressed in grams per cubic centimeter gives a leach unit expressed in terms of the fraction leached $(cm^2/cm^3)^{-1}$ day^{-1} or, as usually written a penetration rate in cm/day. A recent IAEA panel recommended that this penetration unit be used for comparison purposes. However, for long-term comparisons and evaluations a diffusion coefficient is preferable. The fourth unit shown on the slide is a diffusion coefficient (for a semi-infinite slab) that has been shown to be applicable to many waste solids; namely,

$$D = \frac{\pi}{4} \left(\frac{V}{S}\right)^2 \quad m^2 ,$$

if a plot of (a/A_0) versus $t^{1/2}$ is a straight line. where a is amount of an ion leached in time t, A_0 is total amount of an ion in the sample, S is total area of exposed surface of sample. V is volume of sample, and m is the slope from the plot of (a/A_0) versus $t^{1/2}$. Using a diffusion coefficient the effect of shape and radioactive decay may be accounted for mathematically by substituting the appropriate geometry factors and decay constant $(A = A_0 e^{-\lambda t})$ into the diffusion equations — Fick's first and second laws.

SLIDE 26 Typical Leach Factors and Diffusion Coefficients for ^{137}Cs and ^{106}Ru from Products Incorporating Waste Solids (69-9263)

This slide shows typical values of leach factors (g cm^{-2} day^{-1}) and diffusion coefficients (cm^2/day) for various waste solids incorporated in glass, ceramic solid, polyethylene, and asphalt. Note that leach factors which are not calculated from data obtained under identical conditions (exposed surface, volume, temperature) can give misleading information. For example, the leach factors indicate that ^{137}Cs is leached twice as fast from the ceramic product as from the polyetlylene product (4.7×10^{-4} vs 2.0×10^{-4}). However, when geometry factors are taken into account by using the diffusion coefficients, it may be seen that ^{137}Cs is leached about 4.5 times as fast from the polyethylene product as from the ceramic (1.7% vs 0.38% in 30 yrs). The results on this slide also show that glasses, as you would expect, are much more insoluble than other disposal media. Also it shows that a soluble ion, ^{137}Cs, is leached more readily from the same product than an insoluble ion, ^{106}Ru.

SLIDE 27 Leach Rates of Asphalt Products Incorporating Simulated ORNL Intermediate Level Waste (66-11009 RI)

Asphalt products containing 20, 40, and 60 wt % solids from ORNL ILW were leached with water for periods of up to 16 months. The simulated wastes in these studies contained tracer levels of radioactivity – that is, 0.1 microcurie of ^{137}Cs or ^{106}Ru per ml. The sodium and ^{137}Cs are representative of radionuclides that are soluble in alkaline wastes which can contain carbonate, sulfate, or phosphate, whereas the ^{106}Ru is representative of insoluble radionuclides (as mentioned before). The latter include strontium and rare earths. Generally, the leach rates of asphalt products were lower, by a factor of 50 to 100, than those of cement products containing similar amounts of waste salts. The leach rates were essentially the same for the other intermediate-level waste solutions (ACS or 2CW) studied. The introduction of a clay (2%) to adsorb the cesium reduces the leach rate of Cs by 1-2 magnitudes. The presence of 2% water glass holds the clay in suspension. These additives increase the flash point by 65°C.

SLIDE 28 Cross Section of Asphalt Products Containing 60 wt % solids from Simulated ORNL Intermediate-Level Waste (Photo 81049 R1)

This slide shows that bubbles form in the products at an external ^{60}Co dose of about 10^8 rad causing a swelling of up to 30%. With softer asphalt the bubbles can escape. Thus, we think that about 10 curies/gal or about 3 curies/liter may be a practical limit.

SLIDE 29 Leach Rate of Fission Products from the Asphalt (67-8294-R2)

Products containing 60 wt % solids from ORNL ILW, ACS, and 2CW1 and containing from 2 to 52 curies of aged mixed fission products per gallon were prepared from a hard-base asphalt. An ORNL ILW-asphalt product that contained 52 curies per gallon of product showed no gross volume increase or large gas bubbles after an exposure of 4.2×10^7 rads; however, bubbles 1 mm or less in diameter were observed. After an exposure of 2.3×10^7 rads, the ACS-asphalt product was soft and rubbery but contained no bubbles. A few 1/4-in.-diam bubbles could be seen in the hard 2CW1-asphalt product after exposure to 1.8×10^7 rads. No net evolution of gases or swelling has been measured in these internal irradiation tests with hard asphalt which have now reached a dose of 1×10^8 rads (over 838 days) as contrasted to an average 36% volume increase observed with external irradiation at 1×10^8 rads (over 10 days). The difference in irradiation time may be significant – for example, the gases, if formed, may recombine with the asphalt over an 838-day period.

It was concluded that asphalt products show satisfactory physical and chemical stability at irradiation doses of 10^8 to 10^9 rads. Net gas formation and product swelling may occur but can be controlled by using a softer base asphalt.

SAFETY EVALUATION OF SALTS ASPHALT PRODUCT

An assessment was made of the safety aspects of producing and storing asphalt or polyethylene products containing oxidizing salts. The incorporation of inert solids in asphalt does not appear to present any hazard beyond that normally present when an organic material with a high flash point is being processed, stored, or shipped. In fact, the flash point of an asphalt product should increase as the amount of inert solids increases. The hazards caused by incorporating an oxidant (nitrate salts) in asphalt were studied intensively. Tests on the ILW product (60 wt % solids, including 35% nitrate) by the Bureau of Explosives (Association of American Railroads, New York, N. Y) indicated that the material did not fall within any of the classes of dangerous goods as defined by Interstate Commerce Commission regulations.

Standard drop-weight, autoignition, shock sensitivity, and flame-propagation tests of small samples containing 20, 40, and 60 wt % solids from ILW were made. These tests did not show any explosive potential. In standard burning tests with 30-gal-drum samples, the salts-asphalt mixtures burned vigorously, as would be expected, but did not explode or show a significant increase in burning rate over that for pure asphalt. However, the internal temperature in the asphalt mass was not monitored in these tests. The burning characteristics of asphalt or polyethylene containing 40 to 75 wt % sodium nitrate or sodium nitrite were determined with small samples in air. The nitrate-asphalt, nitrite-asphalt, and nitrate-polyethylene samples ignited at 330, 275, and 440°C respectively. The asphalt samples burned vigorously, while the polyethylene samples burned slowly. Studies of phase separation as a function of time and temperature showed that the salts begin to separate from the asphalt at temperatures above 60°C. Therefore, products with power densities as high as 40 Btu hr^{-1} ft^{-3}, which is about eight times the power density of a typical intermediate-level waste concentrate, could be stored in 55-gal drums before phase separation would become a problem. The explosive hazards of the nitrate-asphalt system were studied by detonating blasting jelly in 1- to 2-kg samples of the mixture confined in 4-in. sched 80 steel pipes. Only a sample containing 10 wt % asphalt and 90 wt % $NaNO_3$, with about 50% voids, could be detonated. Irradiation of samples in a ^{60}Co source showed that asphalt-nitrate products could reach 50% void volumes at an absorbed dose of about 10^9 rads; however, polyethylene-nitrate samples showed no signs of voids at this dose. It was concluded that asphalt and polyethylene are good media for incorporating intermediate-level radioactive wastes that do not contain oxidizing materials. Incorporation in asphalt is not recommended for wastes containing oxidants. Polyethylene may be acceptable for this purpose. Further studies would be required to fully assess the safety of the system.

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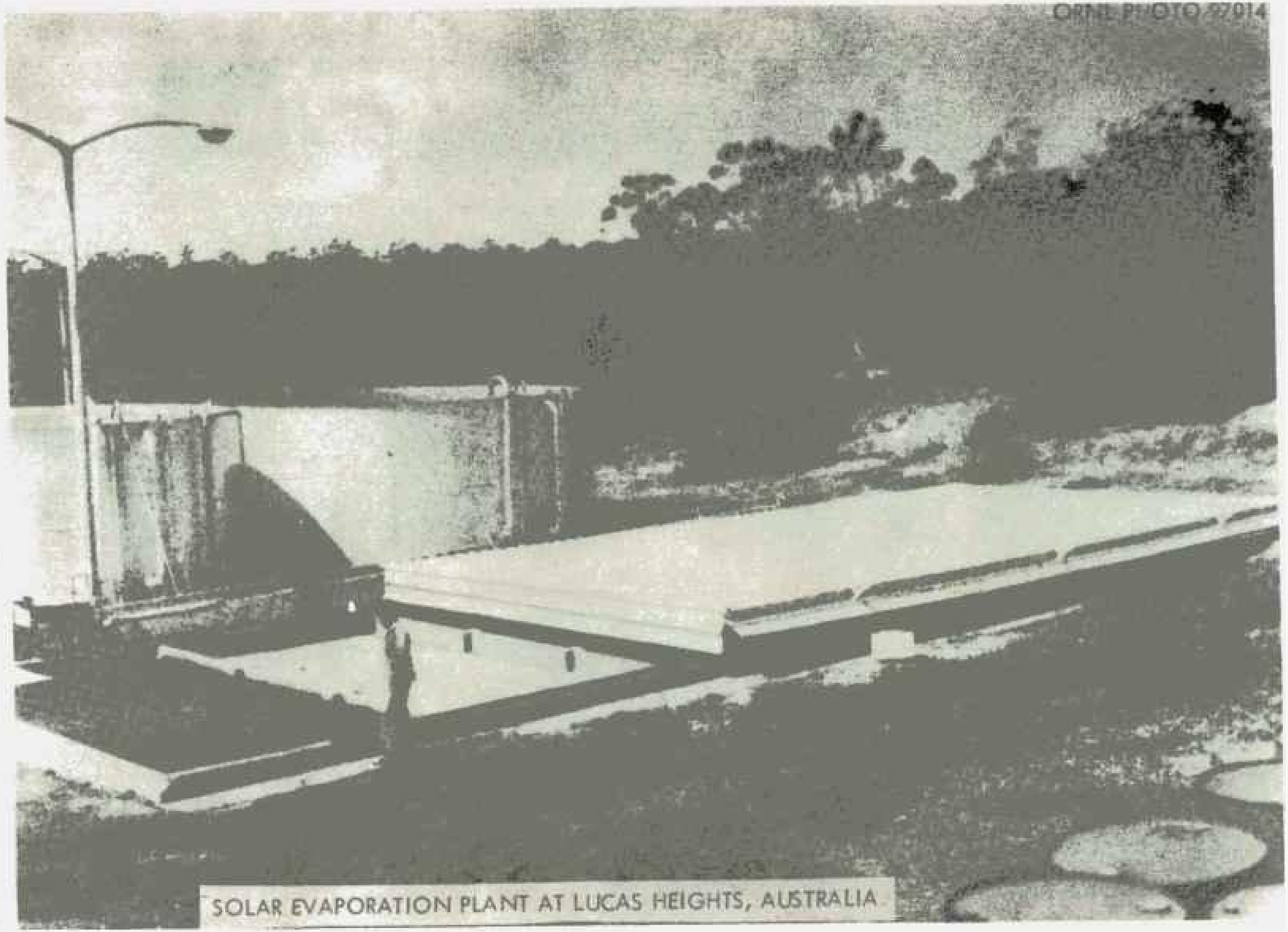
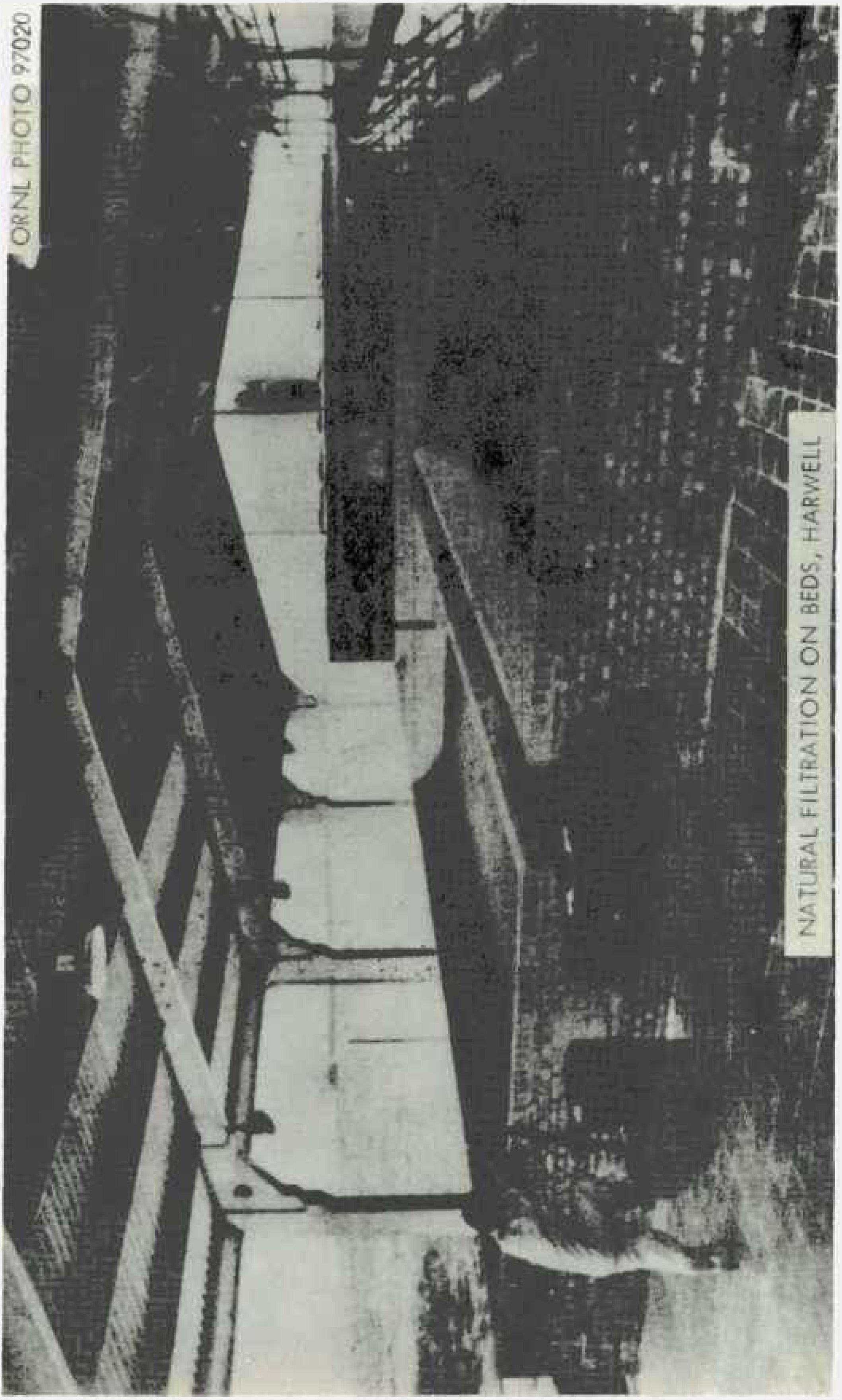


ORNL PHOTO 97014

SOLAR EVAPORATION PLANT AT LUCAS HEIGHTS, AUSTRALIA



ORNL PHOTO 97020

NATURAL FILTRATION ON BEDS, HARWELL

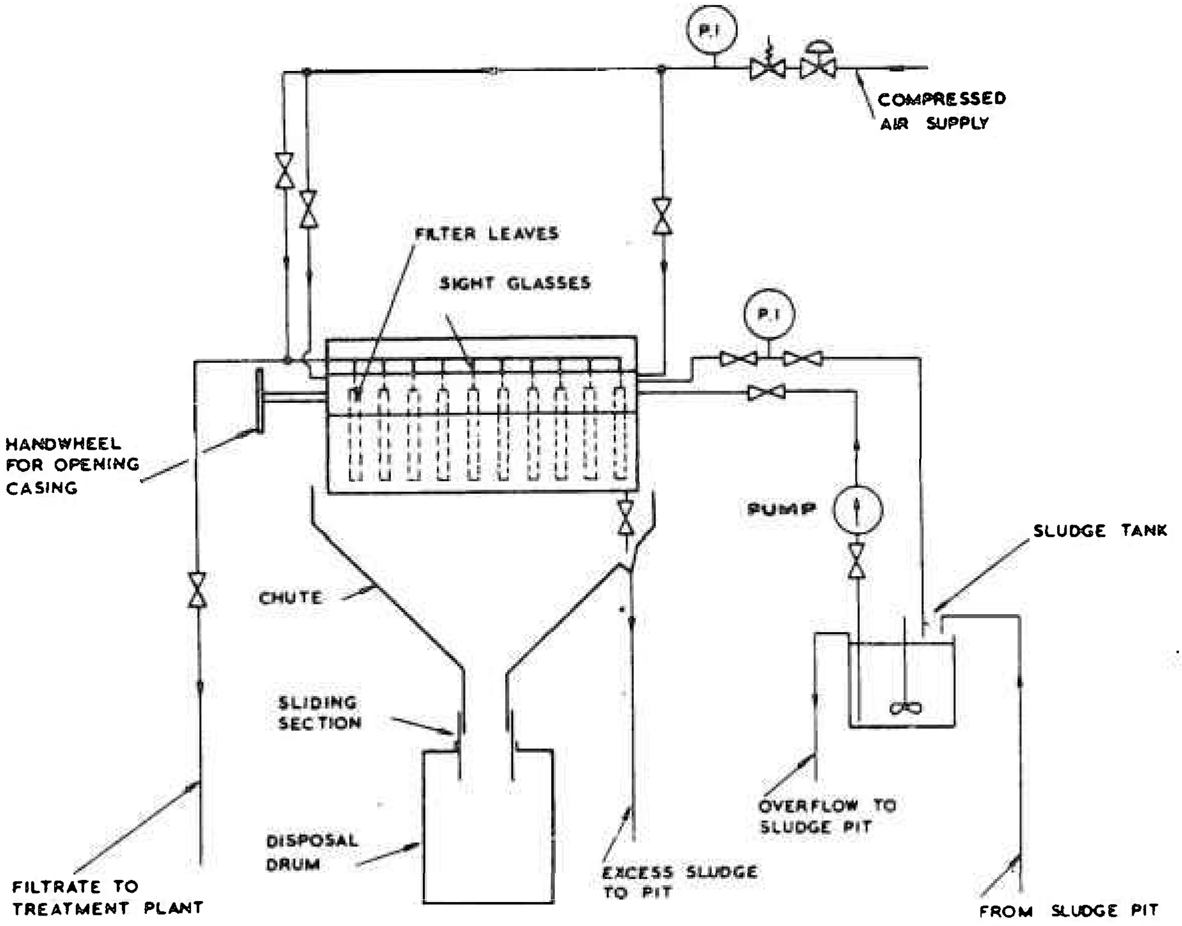
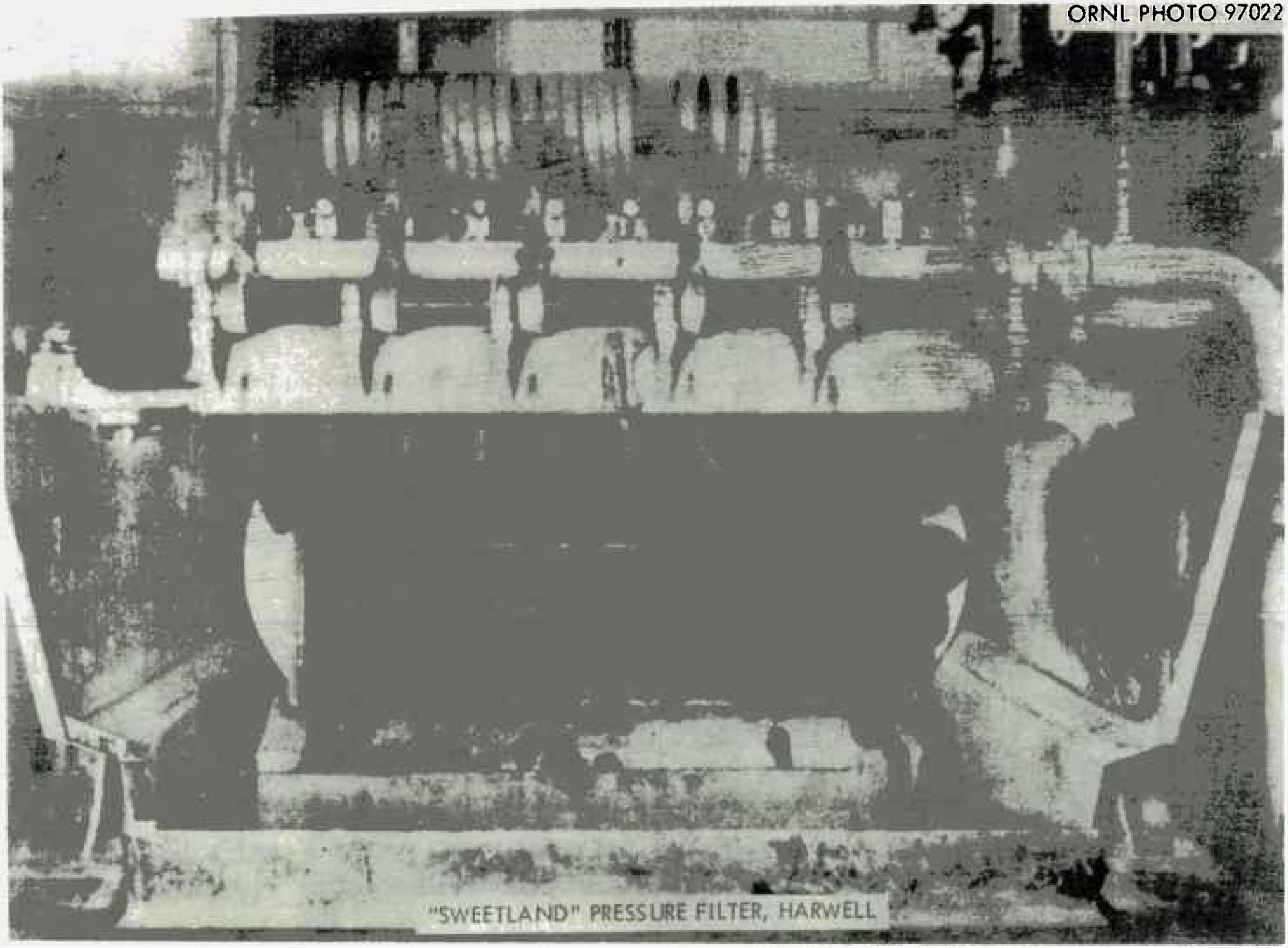
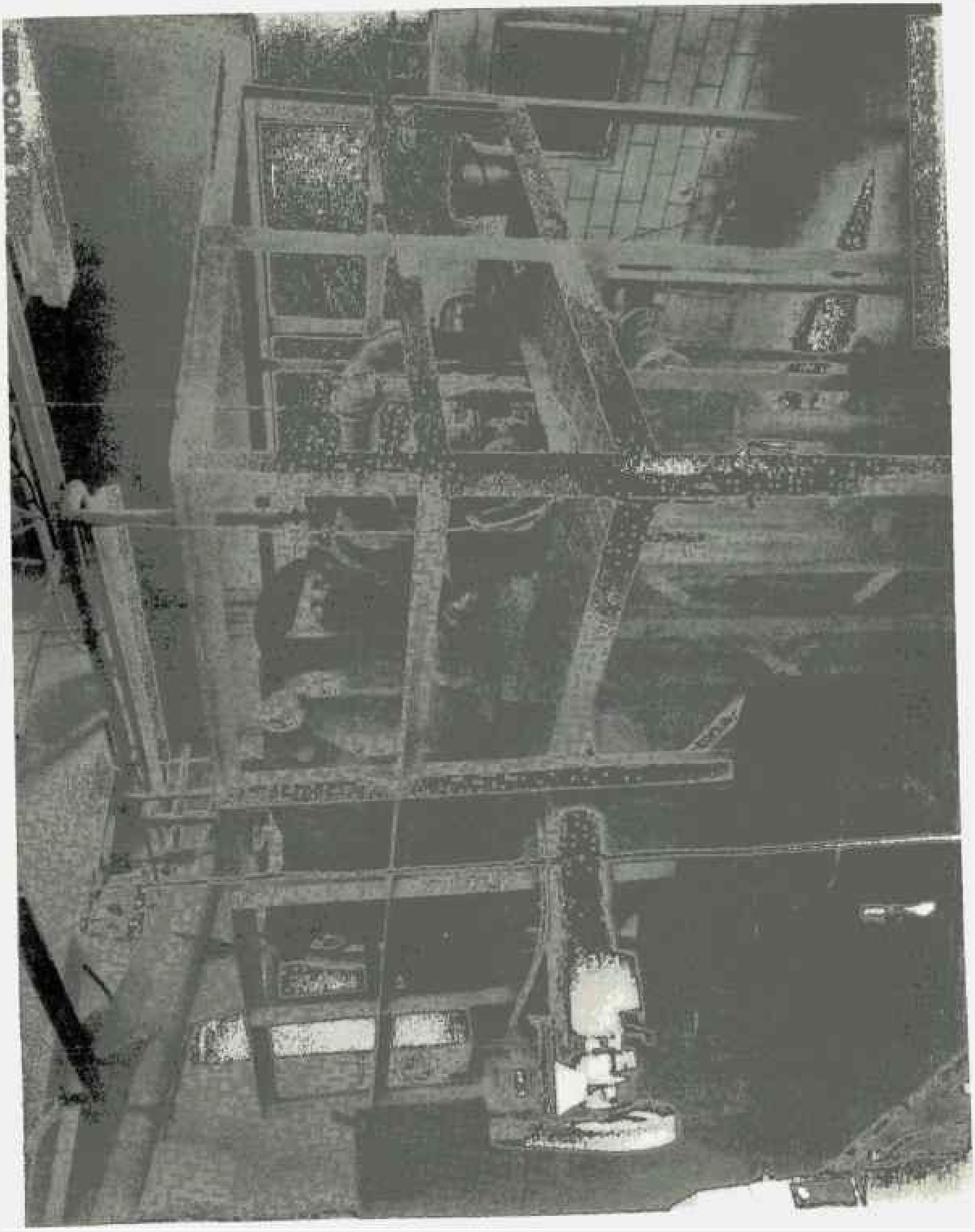


DIAGRAM OF "SWEETLAND" FILTER CIRCUIT, HARWELL

ORNL PHOTO 97022

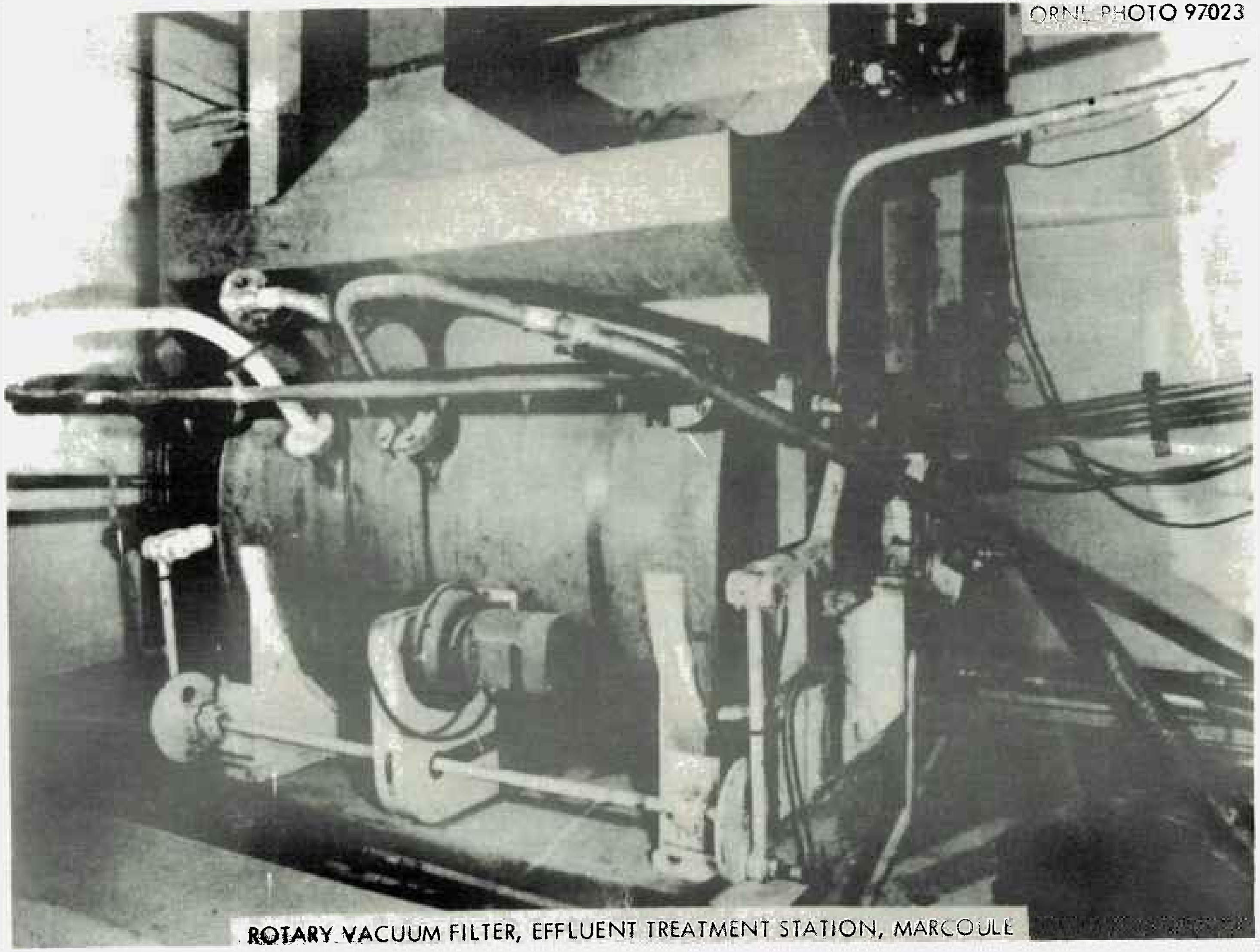


"SWEETLAND" PRESSURE FILTER, HARWELL



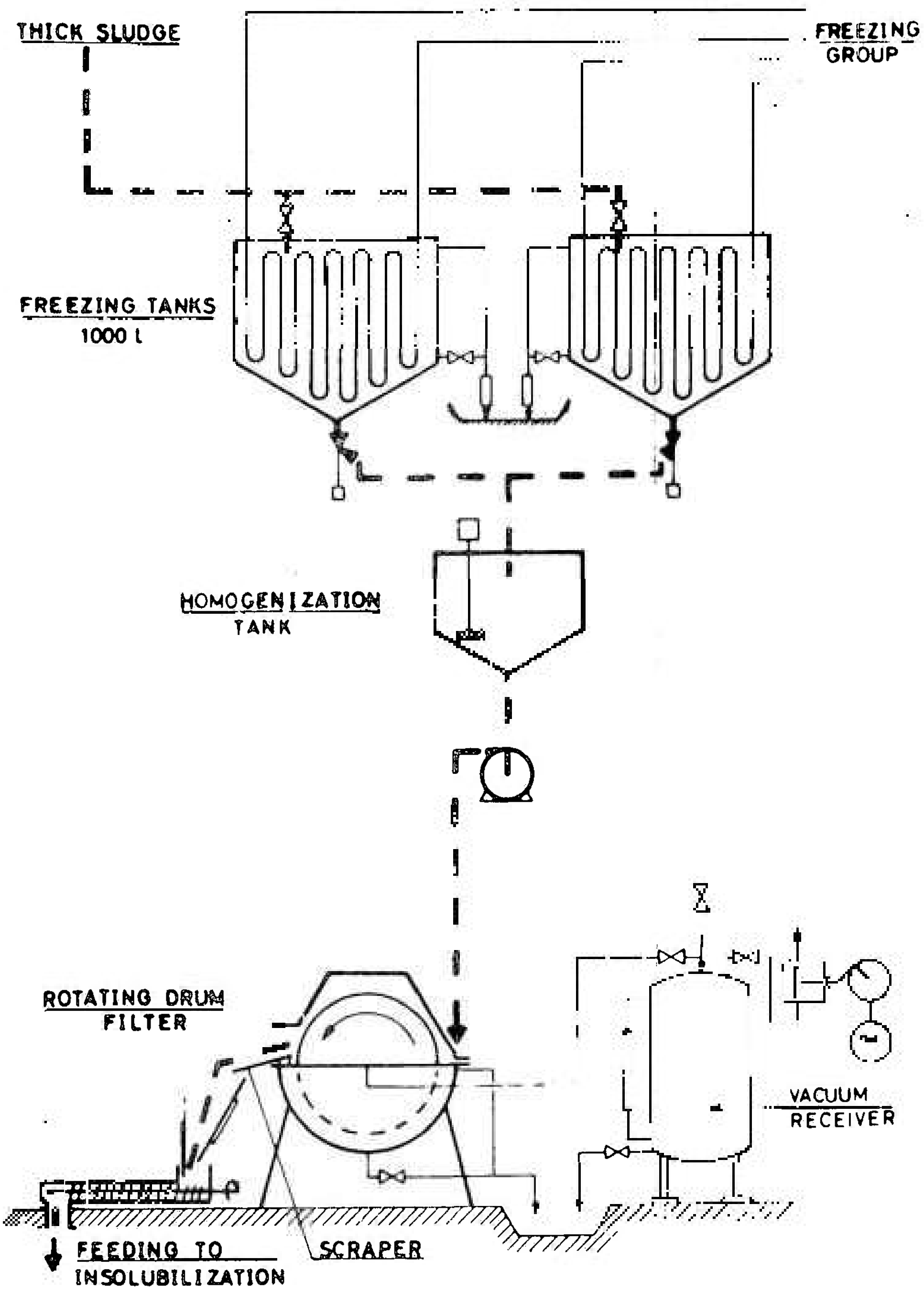
ORNL PHOTO 97021

VACUUM FILTER, PRECOATED WITH DIATOMACEOUS EARTH, LOS ALAMOS



ORNL PHOTO 97023

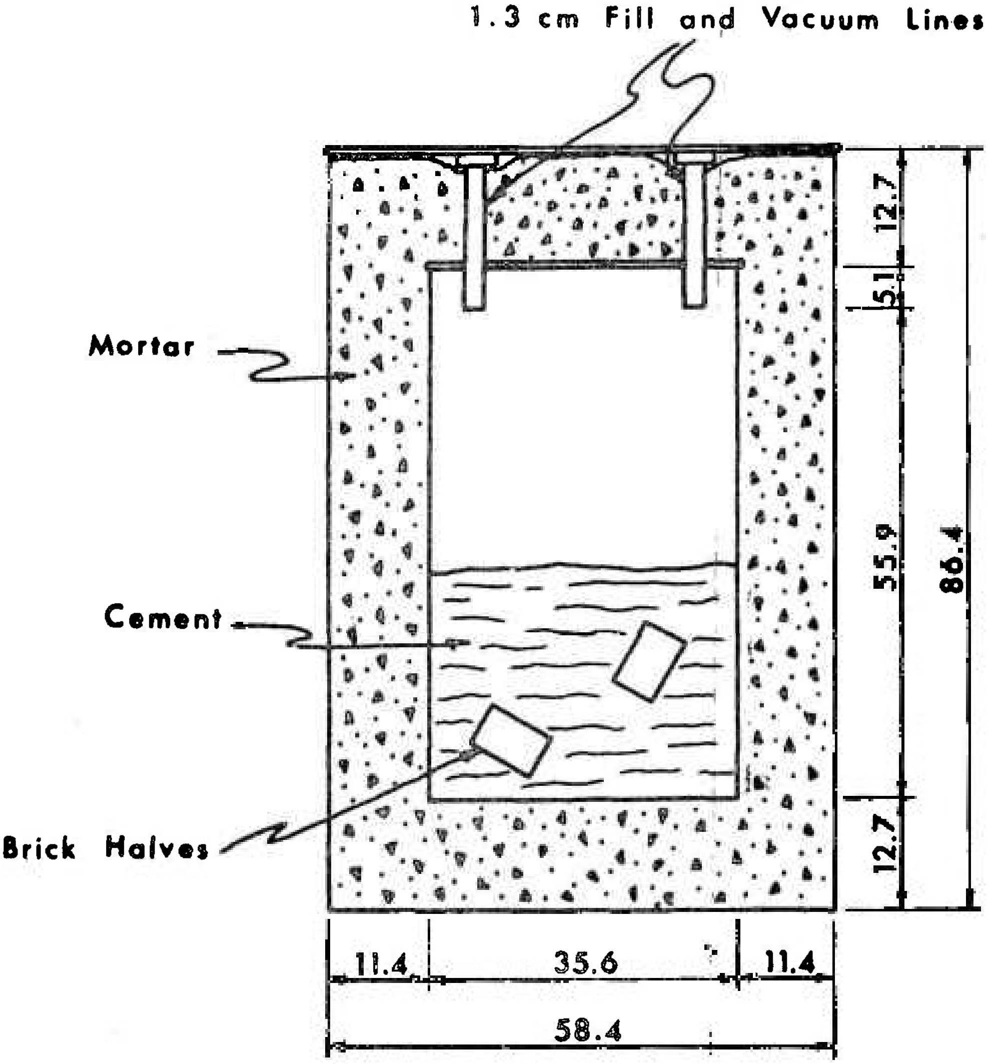
ROTARY VACUUM FILTER, EFFLUENT TREATMENT STATION, MARCOULE



FREEZE-THAW VACUUM FILTRATION UNIT, MOL

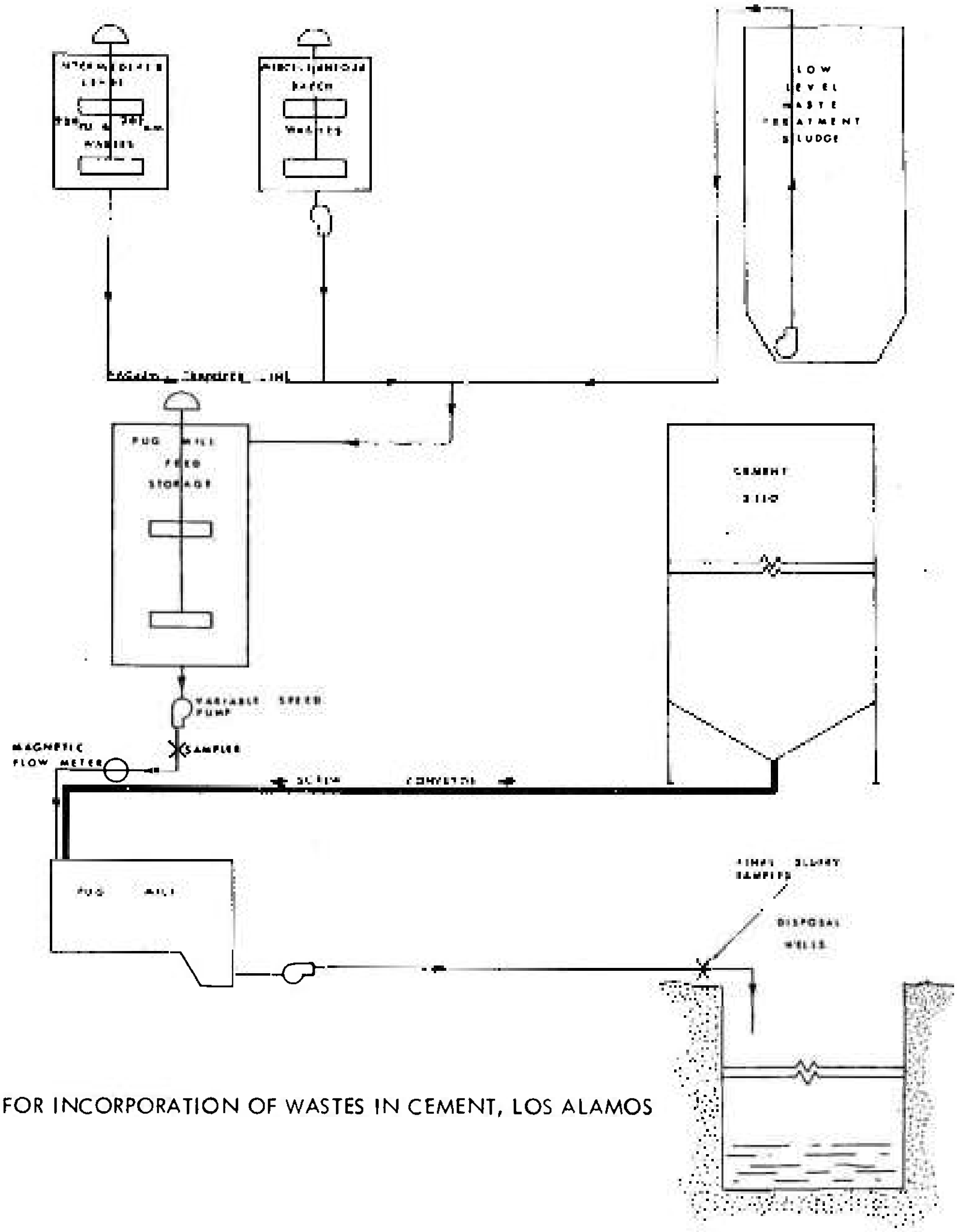
VOLUME REDUCTION DURING SUCCESSIVE STEPS OF TREATMENT AT MOL

	Low Activity (m^3)	Intermediate Activity (m^3)
Raw laboratory effluent	1000	1000
Sludge at outlet of flocculator	3.2	47.7
Sludge after settling (4% solids); inlet of freezing plant	1.5	6.5
Sludge after freeze-thaw and vacuum filtration, 35 to 40% solids	0.35	1.54
Sludge after disposal into bitumen (final volume of concentrate)	0.11	0.47
Total concentration factor	9100	2100
Sludge concentration factor	14	14

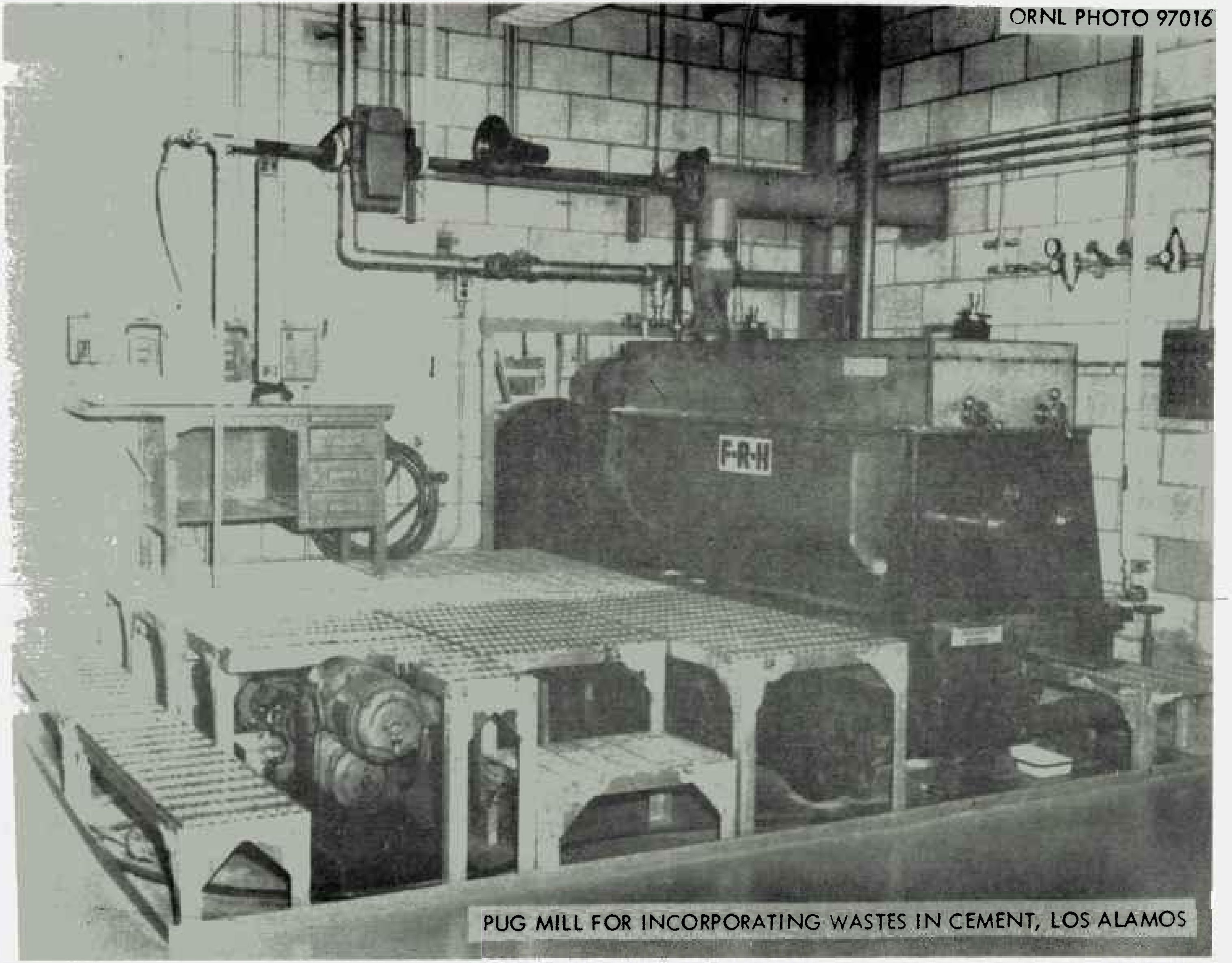


Note: All dimensions in cm

DRUM USED FOR FINAL DISPOSAL, LOS ALAMOS

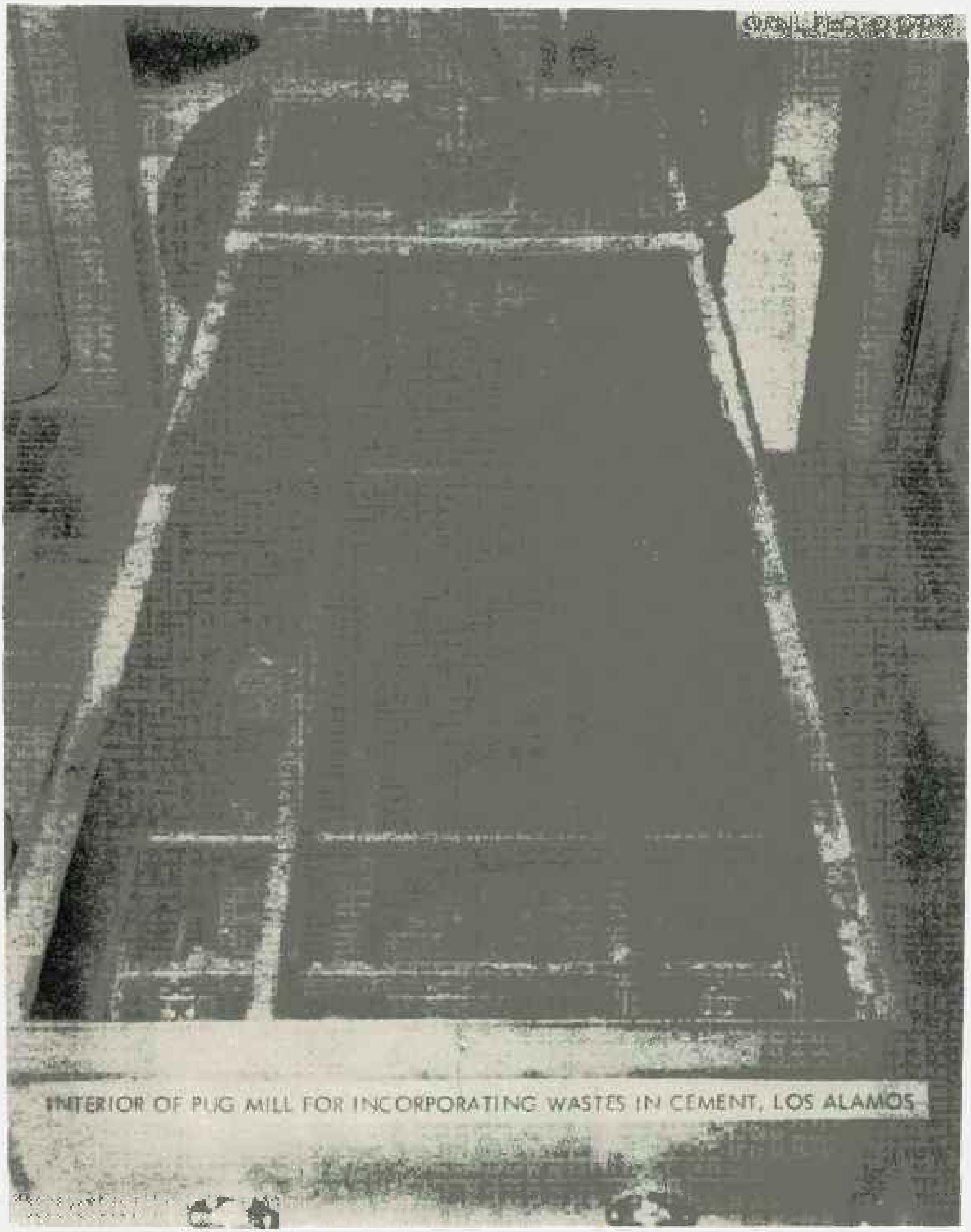


FLOWSHEET FOR INCORPORATION OF WASTES IN CEMENT, LOS ALAMOS

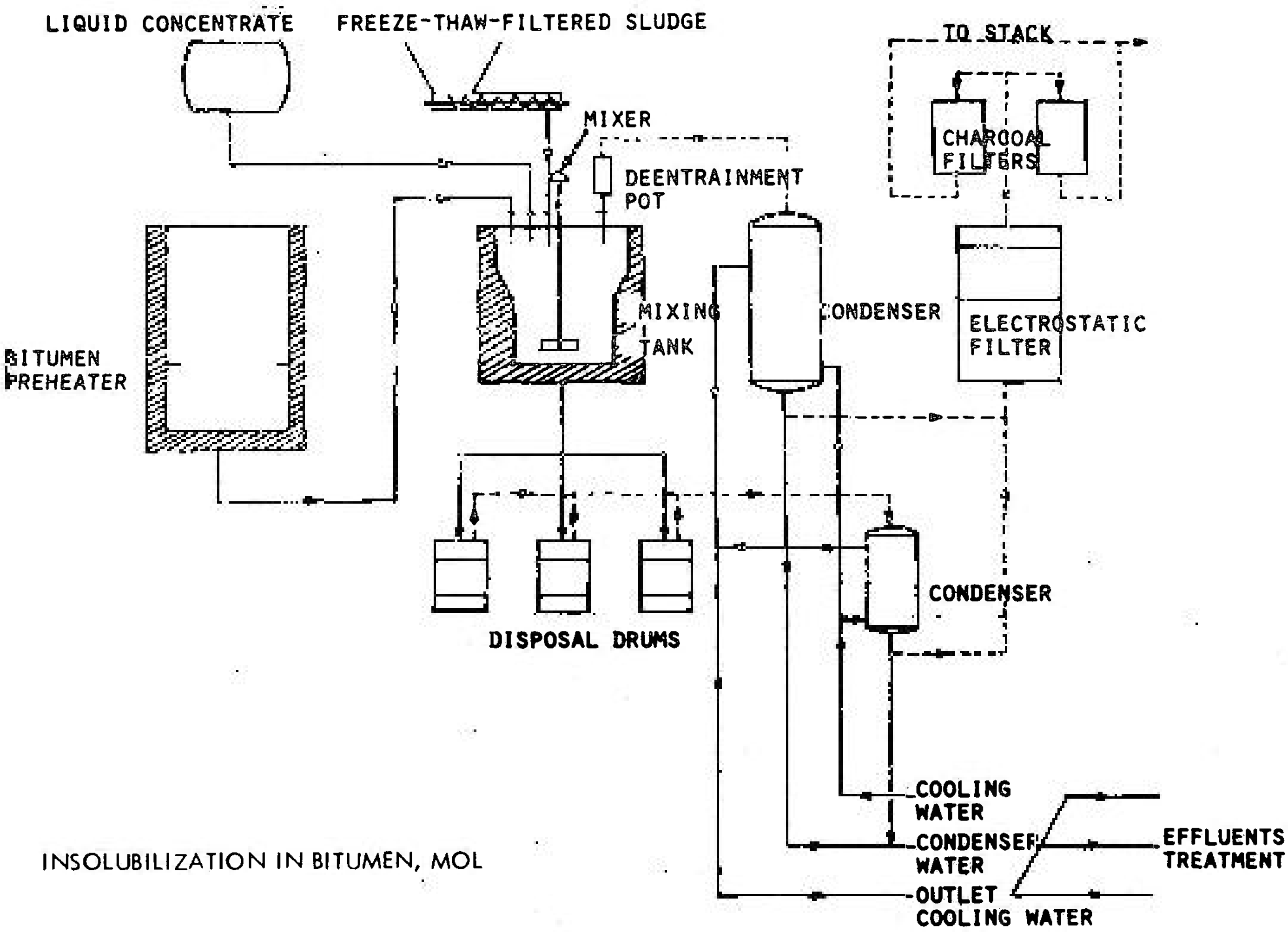


ORNL PHOTO 97016

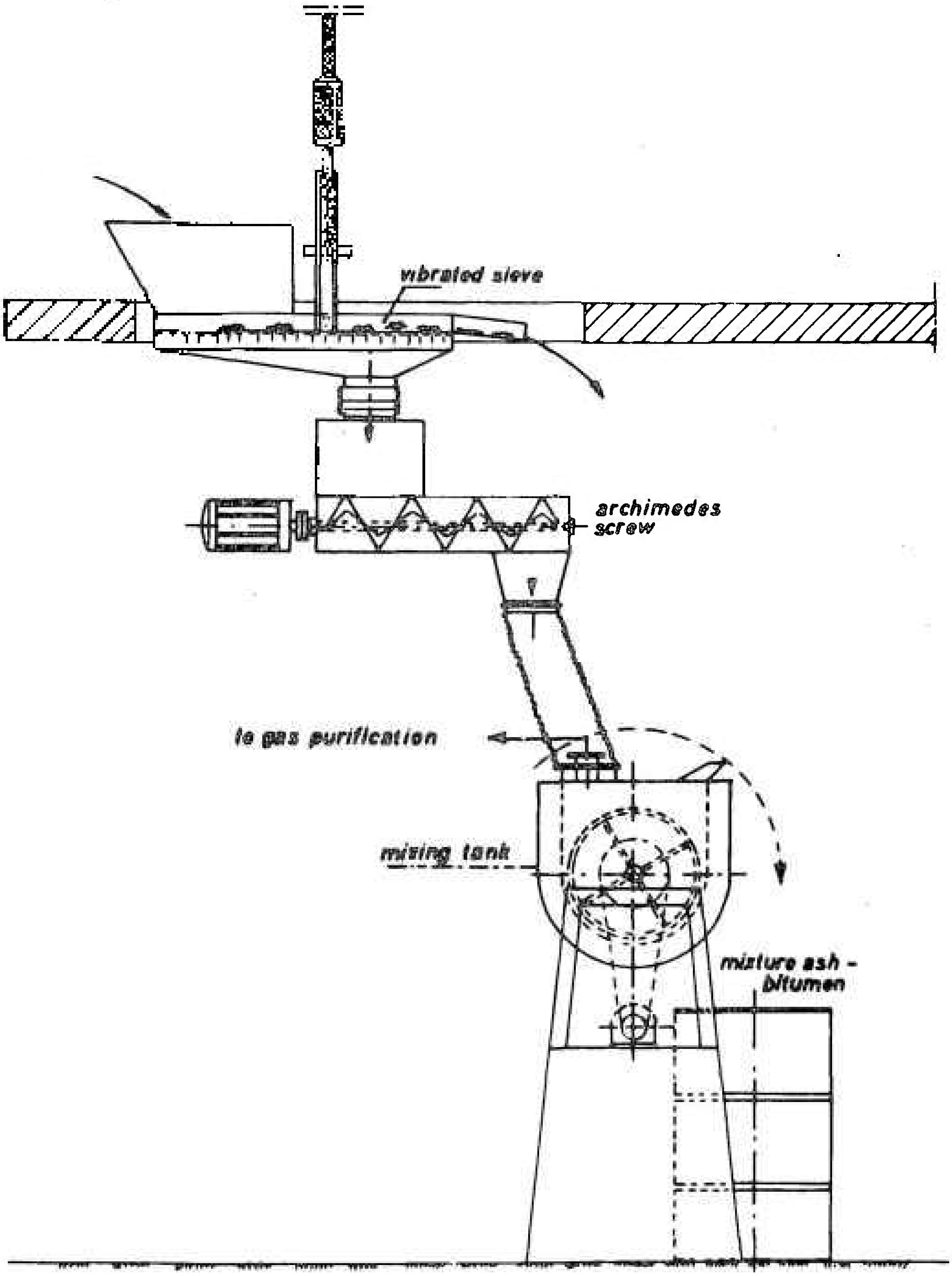
PUG MILL FOR INCORPORATING WASTES IN CEMENT, LOS ALAMOS



INTERIOR OF PUG MILL FOR INCORPORATING WASTES IN CEMENT, LOS ALAMOS

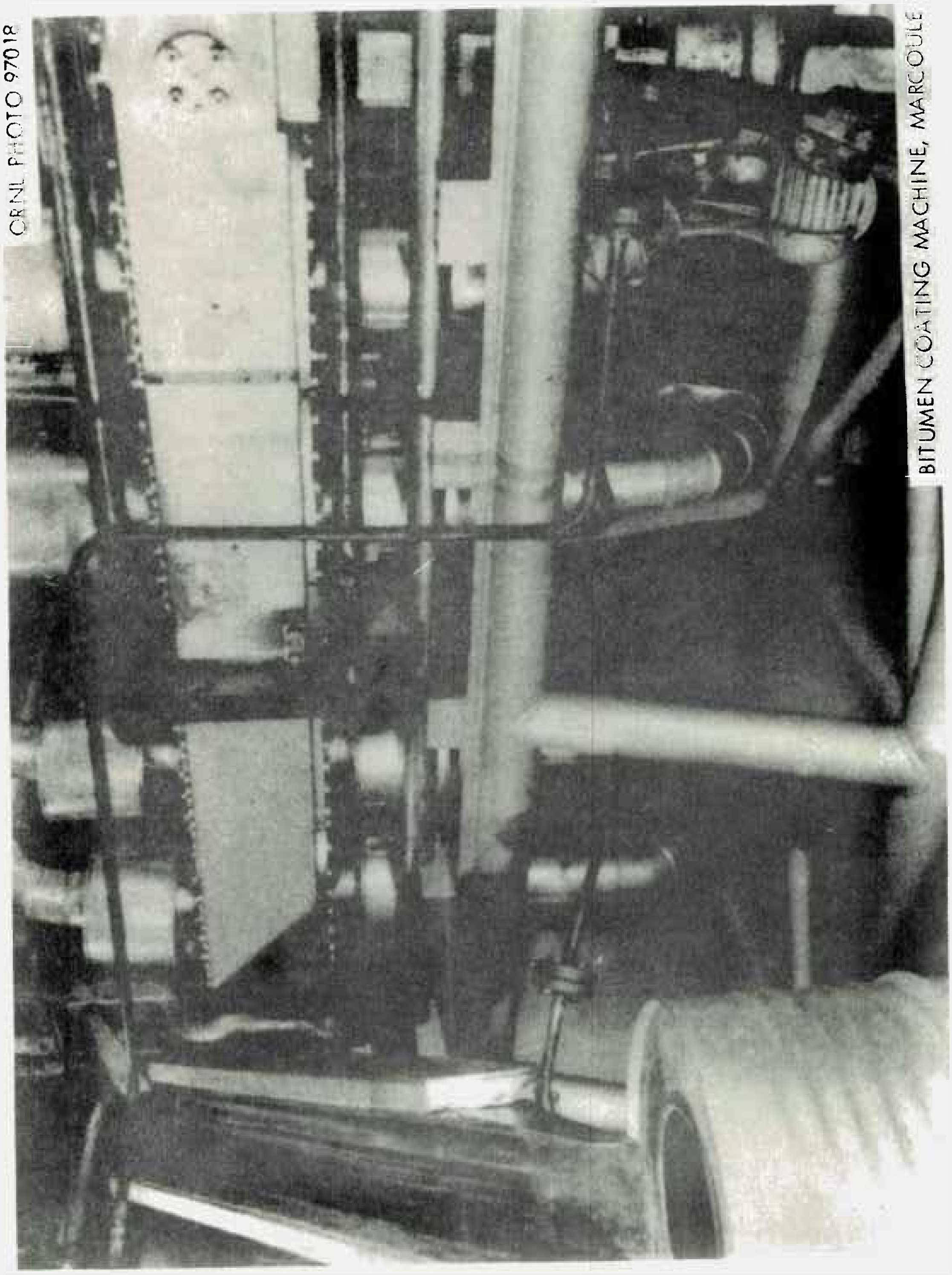


INSOLUBILIZATION IN BITUMEN, MOL



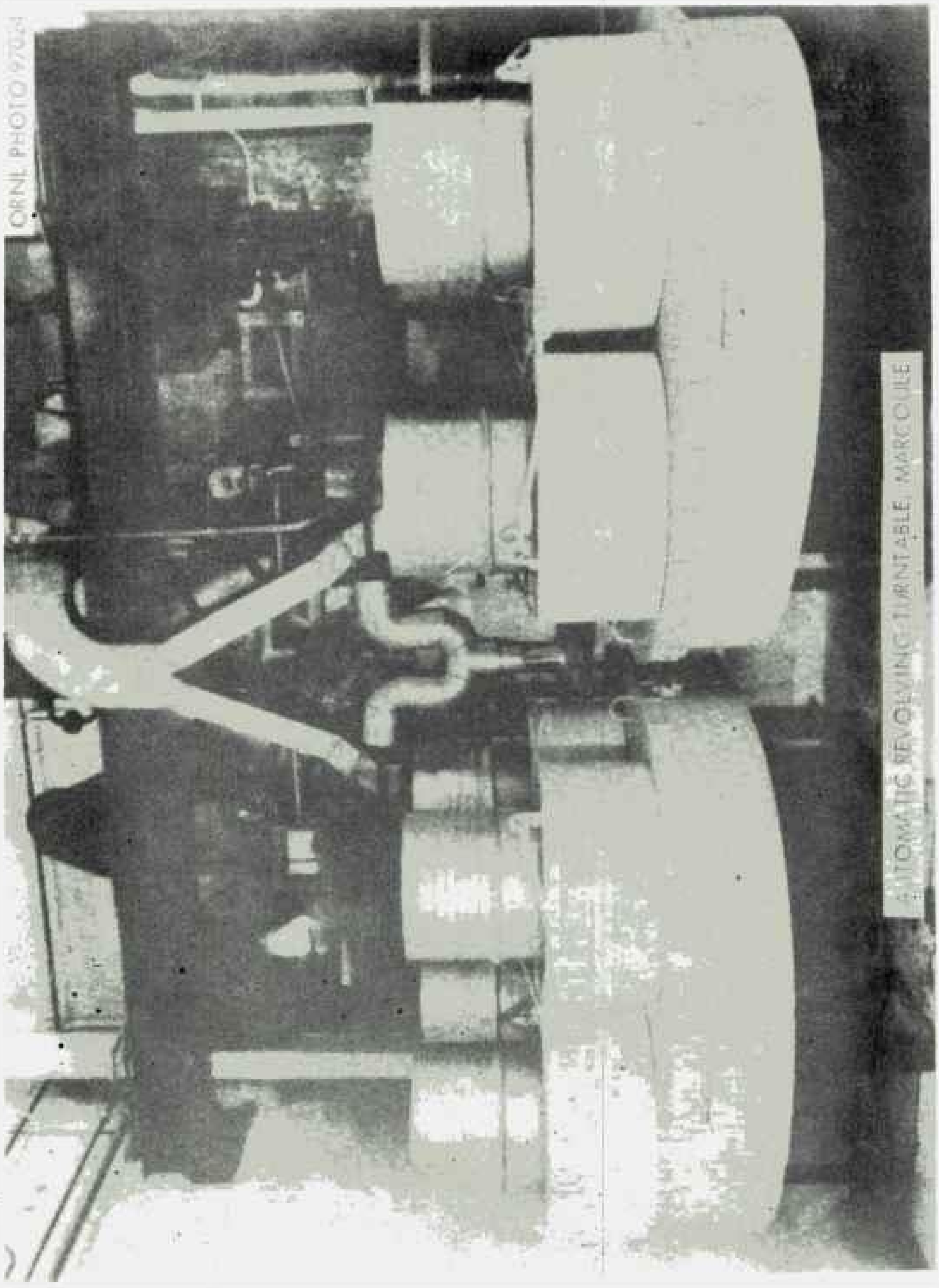
INSTALLATION FOR INSOLUBILIZATION OF ASH AND VERMICULITE, MOL

ORNL PHOTO 97018



BITUMEN COATING MACHINE, MARCOULE

VARIOUS DETAILS OF COATING MACHINE, MARCOULE



ORNL PHOTO 9742

AUTOMATIC REVOLVING TURNTABLE, MARCOULE

WASTE RESIDUES WHICH HAVE BEEN INCORPORATED IN ASPHALT AND/OR POLYETHYLENE

CHEMICAL SLUDGES:

$Ca_3(PO_4)_2$
$Fe(OH)_3$
$Cu_2Fe(CN)_6$
$Ni_2Fe(CN)_6$
$Ca(BO_2)_2$
$Ca(OH)_2$
$CaCO_3$

CONCENTRATED SALT SOLUTIONS:

$NaNO_3$
$NaAlO_2$
Na_2SO_4
$NaBO_2$
Na_3PO_4
$NaOH$

ION EXCHANGE MATERIAL:

Synthetic organic resins
Synthetic inorganic zeolites
Natural inorganic zeolites

ORGANIC SOLVENTS:

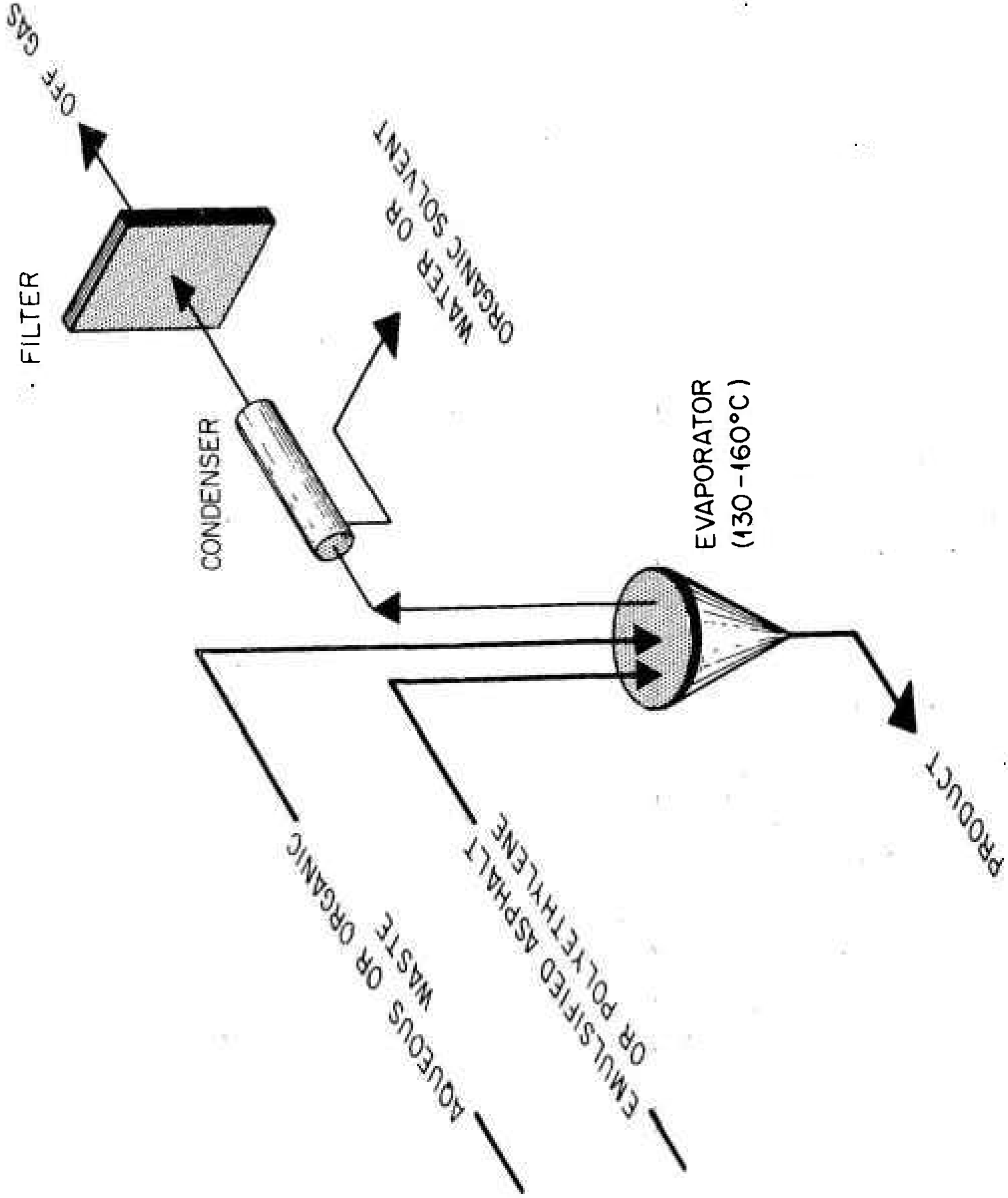
CCl_4
Cl_2CCCl_2
$\underline{n}$ - $C_{12}H_{26}$
$(C_4H_9)_3PO_4$

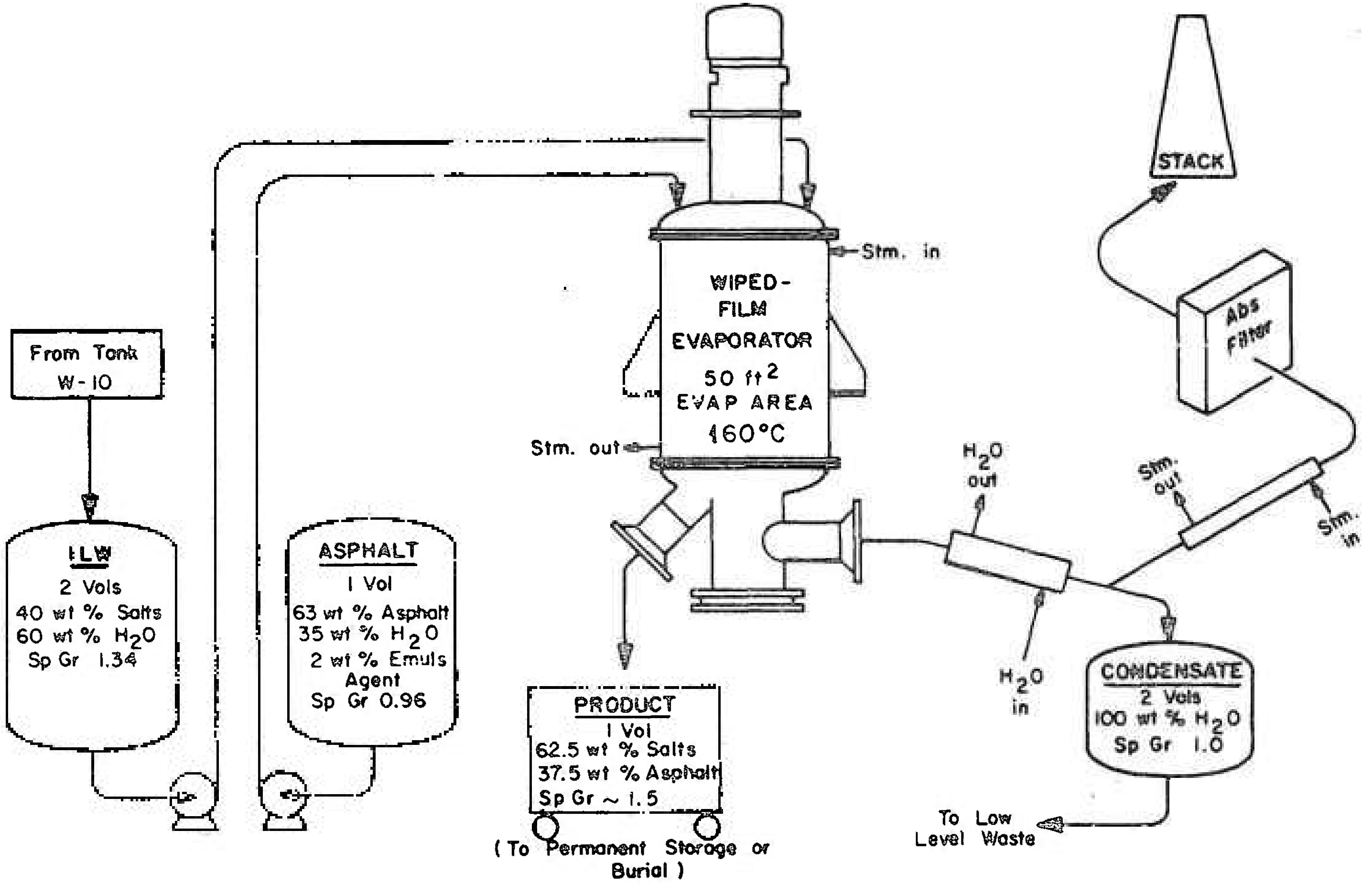
INCINERATOR ASH:

Silicates		sodium
Oxides	of	calcium
Carbonates		aluminum
Phosphates		magnesium
		iron

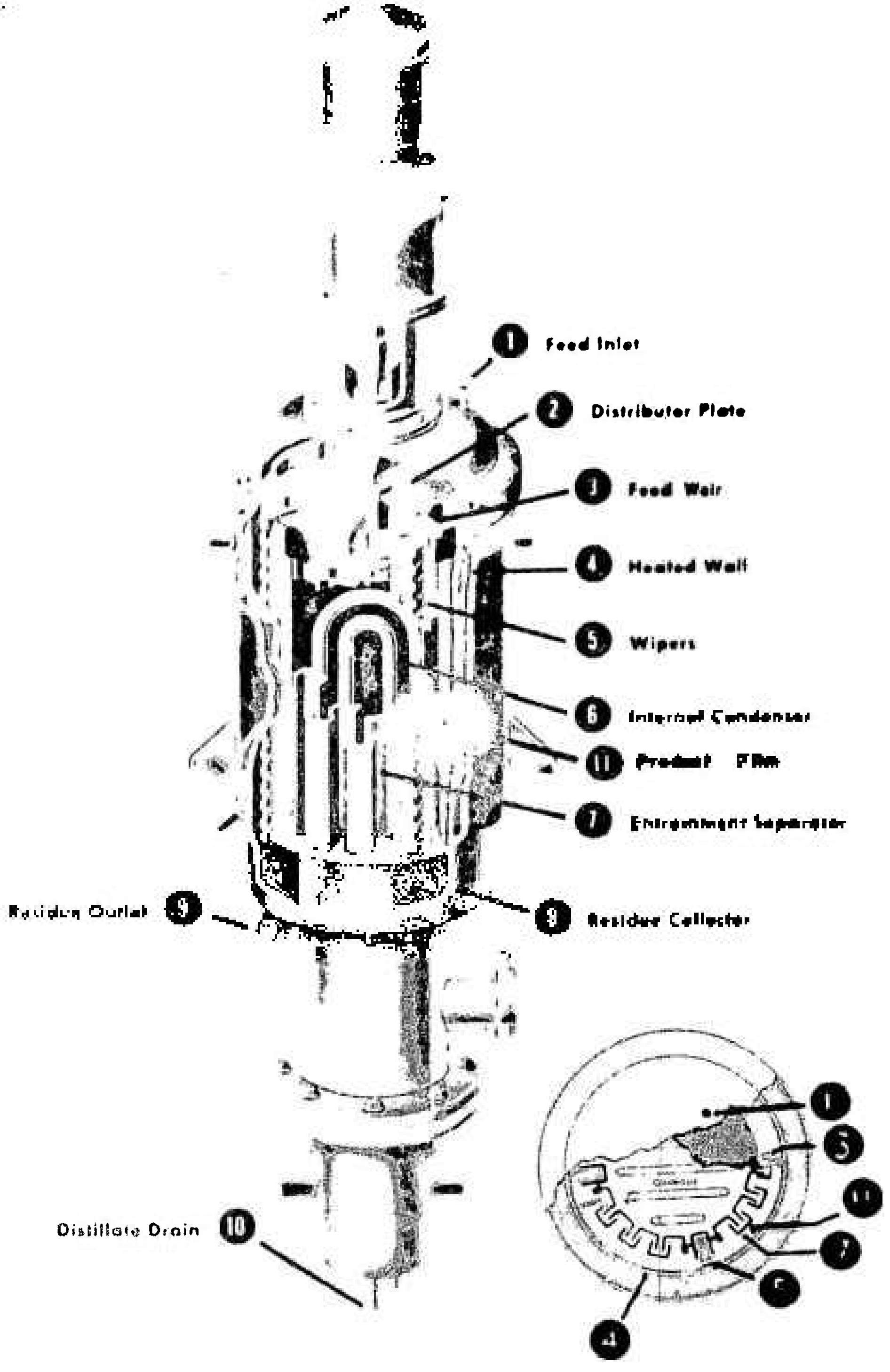
PLASTIC WASTES:

Polyvinyl chloride
Polyethylene
Polystyrene

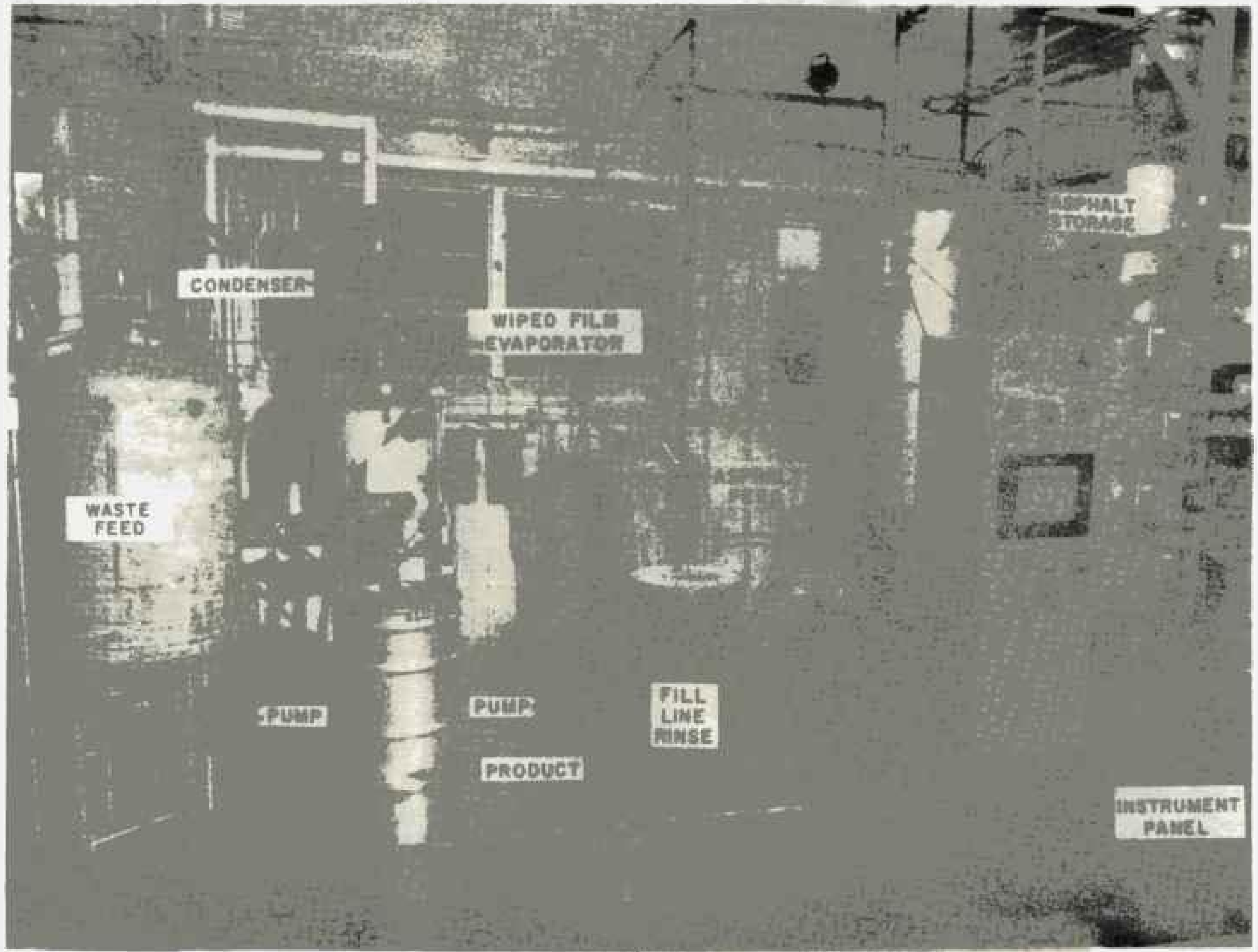

OFF GAS
FILTER
WATER OR ORGANIC SOLVENT
CONDENSER
EVAPORATOR (130-160°C)
AQUEOUS OR ORGANIC WASTE
EMULSIFIED ASPHALT OR POLYETHYLENE
PRODUCT



ORNL ASPHALT-WASTE SALTS PROCESS


1 Feed Inlet
2 Distributor Plate
3 Feed Weir
4 Heated Wall
5 Wipers
6 Internal Condenser
11 Product Film
7 Entrainment Separator
8 Residue Collector
Residue Outlet 9
Distillate Drain 10
1
5
11
7
6
4

ORNL PHOTO 84202-A



WASTE-ASPHALT PROCESS INSTALLATION

COMPOSITIONS OF SIMULATED ORNL INTERMEDIATE-LEVEL WASTE (ILW) SOLUTION AND AN ASPHALT PRODUCT INCORPORATING SOLIDS FROM ILW

Component	ILW Solution (Molarity)	Asphalt Product[a] (Weight Percent)
Sodium	6.61	18.5
Nitrate	4.64	34.9
Hydroxide	2.06	3.8
Sulfate	0.35	4.1
Aluminum	0.22	0.7
Ammonium	0.19	--
Chloride	0.056	0.2
Asphalt	--	37.8
Density at 25° C	1.34 g/ml	1.5 g/ml

[a] Volume reduction = $\frac{\text{Volumes ILW}}{\text{Volumes Product}} = 2.$

COMPOSITIONS OF SIMULATED WASTES AND SALTS-ASPHALT PRODUCTS IN EMULSIFIED WASTE INCORPORATION STUDIES AT ORNL

(Only a portion of this data is shown on slide 65-12137.)

	Waste Type				Product Type		
	ILW[a]	ACS[b]	2CW[c]	2CW1[d]	ILW	ACS	2CW1
Component	(M)	(M)	(M)	(M)	(wt %)	(wt %)	(wt %)
Na^+	6.61	4.16	0.64	6.64	18.5	16.6	17.1
NH_4^+	0.19	-	-	-	-	-	-
H^+	-	-	6.2	-	-	-	-
Al^{3+}	0.22	-	-	-	0.7	-	-
Fe^{3+}	-	-	0.54	0.37	-	-	2.4
NO_3^-	4.64	2.2	6.2	4.26	34.9	23.7	29.6
OH^-	2.06	0.06	-	1.94	3.8	0.2	3.7
AlO_2	-	1.9	-	-	-	19.5	-
Cl^-	0.056	-	-	-	0.2	-	-
SO_4^{2-}	0.35	-	1.13	0.78	4.1	-	8.3
Density at 25°C (grams per ml)	1.34	1.21	1.31	1.33	-	-	-
Total solids in waste (wt %)	39.1	28.5	38.8	39.4	-	-	-
Asphalt	-	-	-	-	37.8	40.0	39.0
Volume reduction[e]	-	-	-	-	1.8	2.5	1.7

---

[a] ORNL intermediate-level waste solution (evaporator concentrates).

[b] Solution from dissolution of aluminum cladding with $NaOH-NaNO_3$.

[c] Purex second-plutonium-cycle waste. This acid solution is made basic before incorporation in asphalt.

[d] Purex second-plutonium-cycle waste with 455 ml. of 51.5% NaOH added to each liter of 2CW.

[e] Volume reduction is defined as volumes of waste processed per unit volume of product obtained.

LEACH RATES

$$\text{fraction leached per specific area per day} = \frac{\dfrac{(\text{total cts leached})/\text{day}}{(\text{total initial cts})}}{\dfrac{(\text{sample area, cm}^2)}{(\text{sample weight, g})}} = 1.2 \times 10^{-4} \text{ fraction leached } (\text{cm}^2/\text{g})^{-1} \text{ day}^{-}$$

$$\text{Penetration rate} = \frac{\dfrac{(\text{total cts leached})/\text{day}}{(\text{sample area, cm}^2)}}{\dfrac{(\text{total initial cts})}{(\text{sample weight, g})}} = 1.2 \times 10^{-4} \text{ g cm}^{-2} \text{ day}^{-1}$$

$$\text{Penetration rate (including density)} = 1.2 \times 10^{-4} \frac{(\text{g})(\text{cm}^3)}{(\text{cm}^2)(\text{day})(1.2 \text{ g})} = 1.0 \times 10^{-4} \text{ cm/day}$$

$$\text{Diffusion coefficient} = \frac{\pi}{4}\left(\frac{V}{S}\right)^2 m^2 = \frac{\pi}{4}\left(\frac{100 \text{ cm}^3}{100 \text{ cm}^2}\right)^2 \left(\frac{6 \times 10^{-4} \text{ fraction leached}}{\text{day}^{1/2}}\right)$$

$$= 2.8 \times 10^{-7} \text{ cm}^2/\text{day}$$

TYPICAL LEACH FACTORS AND DIFFUSION COEFFICIENTS FOR ^{137}Cs AND ^{106}Ru FROM PRODUCTS INCORPORATING WASTE SOLIDS

Product	^{137}Cs Leach Factor (g cm^{-2} day^{-1})	^{137}Cs Diffusion Coefficient (cm^2/day)	For a 55-gal Drum of Product Fraction Leached in Years Shown		
			1	30	100
Glass + 26 w/o solids[a]	1.6×10^{-7}	6.6×10^{-13}	1.7×10^{-6}	7.5×10^{-6}	9.4×10^{-6}
Ceramic + 37 w/o solids[b]	4.7×10^{-4}	1.1×10^{-7}	6.8×10^{-4}	3.1×10^{-3}	3.8×10^{-3}
Polyethylene + 20 w/o solids[c]	2.0×10^{-4}	2.1×10^{-6}	3.0×10^{-3}	1.3×10^{-2}	1.7×10^{-2}
Asphalt + 20 w/o solids[d]	1.6×10^{-4}	6.1×10^{-6}	5.1×10^{-3}	2.3×10^{-2}	2.9×10^{-2}
Asphalt + 60 w/o solids[d]	5.0×10^{-4}	3.1×10^{-5}	1.1×10^{-2}	5.1×10^{-2}	6.4×10^{-2}
Asphalt + 60 w/o solids[d]	7.0×10^{-6} (^{106}Ru)	1.8×10^{-8} (^{106}Ru)	1.3×10^{-4} (1/4 yr)	1.8×10^{-4} (1/2 yr)	2.2×10^{-4} (1 yr)

[a] TBP-25 waste [b] Purex waste [c] Borate waste [d] Nitrate waste

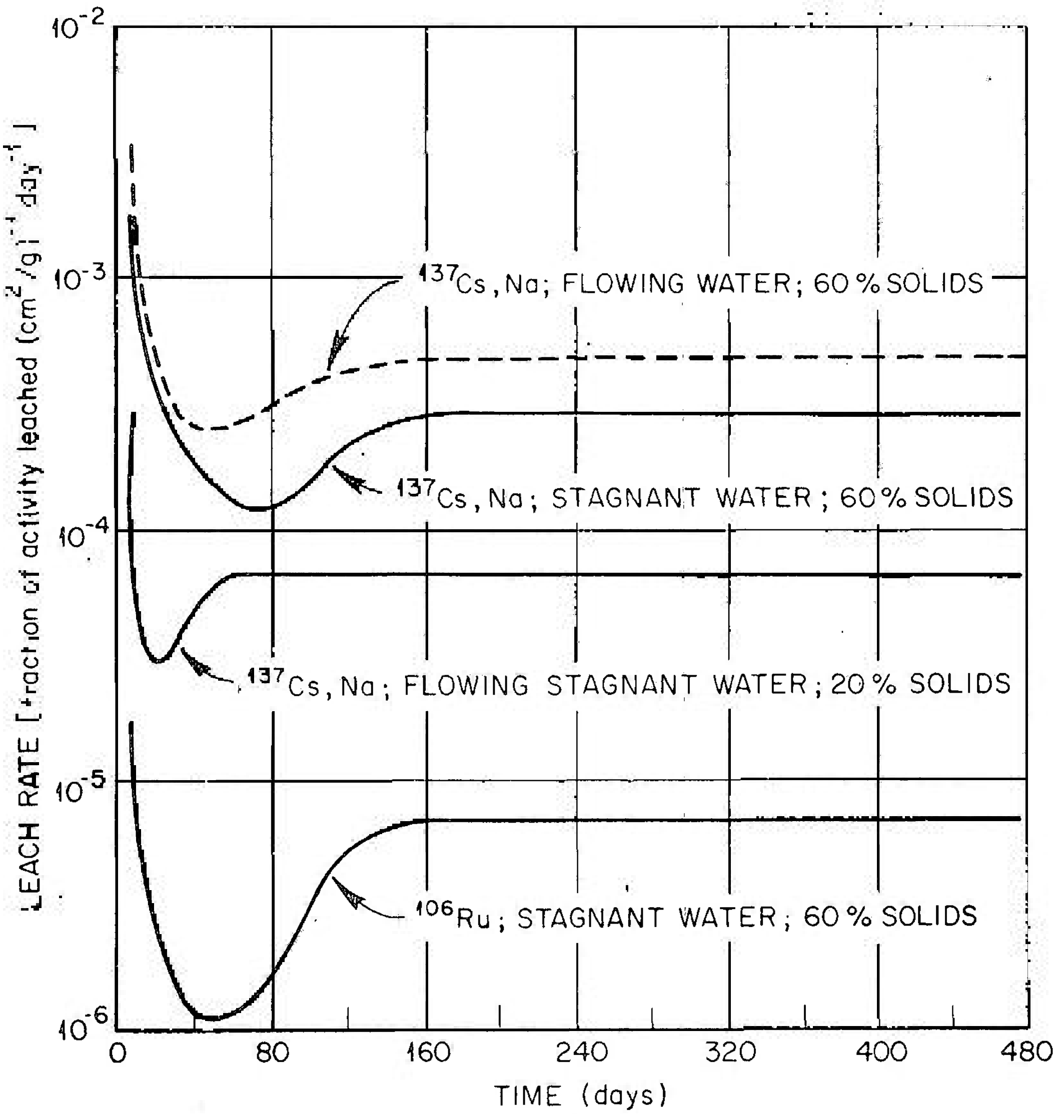

LEACH RATE [fraction of activity leached (cm²/g)⁻¹ day⁻¹]
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
0
80
160
240
320
400
480
TIME (days)
137Cs, Na; FLOWING WATER; 60 % SOLIDS
137Cs, Na; STAGNANT WATER; 60 % SOLIDS
137Cs, Na; FLOWING STAGNANT WATER; 20 % SOLIDS
106Ru; STAGNANT WATER; 60 % SOLIDS

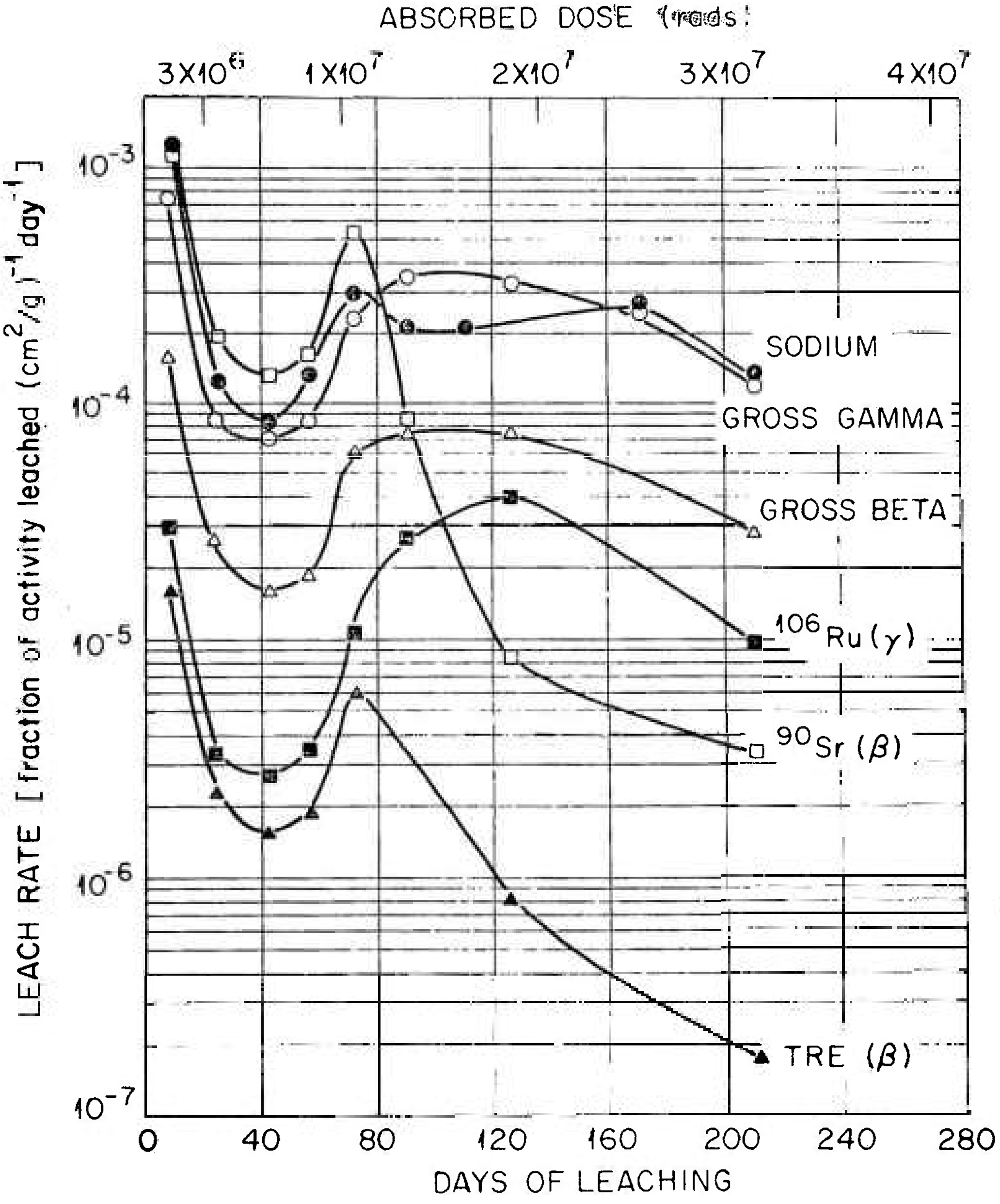
PHOTO 81049R1

(*a*) UNIRRADIATED

(*b*) HARD ASPHALT, 10^7 RADS

(*c*) [illegible]

(*d*) [illegible] ASPHALT, 10^8 RADS


ABSORBED DOSE (rads)
3X10^6
1X10^7
2X10^7
3X10^7
4X10^7
LEACH RATE [fraction of activity leached (cm^2/g)^-1 day^-1]
10^-3
10^-4
10^-5
10^-6
10^-7
SODIUM
GROSS GAMMA
GROSS BETA
106Ru (γ)
90Sr (β)
TRE (β)
0
40
80
120
160
200
240
280
DAYS OF LEACHING

TREATMENT AND DISPOSAL OF SOLID LOW- AND INTERMEDIATE-LEVEL WASTES

R. E. Blanco

The handling and disposal of solid radioactive wastes is often considered of minor importance as compared with the problems associated with liquid and gaseous effluents. This is largely because of the immobility of the wastes. However, large amounts of solid wastes accumulate and their treatment is a significant problem. Perhaps the most difficult problem for individual countries is not the method of treatment but rather the choise of a place for final disposal.

TYPES OF WASTE

SLIDE 1 Types of Solid Wastes (69-10580)

The types of wastes to be expected largely resemble wastes from any laboratory or industrial operation. The volume from the atomic energy industry counterparts is generally greater, however, and often times serviceable items are discarded because of associated radioactivity. The objects vary in size from minute to monstrous; they can be classified as organic or inorganic, as combustible or non-combustible, as compressible or non-compressible, as recoverable or non-recoverable, and as being contaminated by long or by short half-life radioactivity. The classification systems used are determined by the methods of treatment and disposal selected.

COLLECTION

Collection of solid waste is not usually a difficult problem. Frequently normal refuse containers, shielded if necessary, can be used.

Containers should be lined with waxed paper or plastic bags which should be sealed when full. This facilitates removal of the waste and minimizes the spread of contamination.

The number of containers required in a radioactive area will depend, to a certain extent, on the subsequent waste treatment. For example, if incineration is practiced, separate bins for combustible material are advisable. In addition in certain areas the wastes may be incompatible, such as swabs or filter soaked in oxidizing acids and waste material contamined with organic solvents.

Containers should be clearly marked and placed in an accessible place. It is often advantageous to stand the containers in trays to prevent the spread of contamination.

ASSESSMENT OF ACTIVITY LEVELS

It is very difficult to estimate, with any accuracy, the activity level of waste material. This is particularly the case if alpha emitters or soft beta emitters are present. Reliance must be placed on the estimates given by the producers. Each batch collected should be accompanied by a certificate on which a figure for the activity level should be stated together with details of the type of material, the isotopes present and any unusual features.

If the waste contains single radionuclides of known energy, guidance on the probable activity level can be obtained from radiation monitoring. An example is the plutonium drum monitor which is in use at various establishments.

The permissible radiation level on the surface of the container will depend on the subsequent handling methods and, in particular, the time spent by operatives in such operations.

STORAGE

Storage, permanent or for sufficient time to allow decay to acceptable levels, will always be necessary if significant quantities of radioactive material are handled. For such stores adequate shielding must be provided and rain and surface water excluded.

One useful storage method is to employ below ground concrete trenches, covered with at least two layers of removable concrete slabs. It is customary to build walls of inter-locking concrete bricks inside the trenches as and when radiation considerations dictate. This is a more satisfactory arrangement than having individual cells of fixed dimensions owing to the very variable size and radiation level of the waste material.

For certain material steel or ceramic tubes set in a concrete slab serve a useful purpose. These may be set vertically or horizontally. The former are more useful for long-term storage while the horizontal tubes have the advantage of easy transfer and are more satisfactory for short period storage involving more frequent handling.

All open ends of storage tubes should be fitted with removable concrete or lead plugs, and it is often desirable to extract the air from tubular storage and filter it before discharge.

A higher degree of shielding can be obtained by the use of barytes concrete instead of the normal variety.

Material stored should, as far as possible, be in a container, which facilitates removal from the store and controls the spread of contamination.

A suitable method of loading vertical tubes and retrieving the material is by the use of a vacuum pump and suction pad.

SLIDE 2 Sorting Operations in Sealed Area at Harwell (Photo 97220)

Depending on the subsequent treatment of the waste, the material may have to be sorted into various categories. Separation of combustible matter is often practiced and there may be advantages in segregating glass and plastic material. Sorting also affords an opportunity to recover valuable material which has got into the waste by accident.

Sorting is normally carried out in glove boxes of conventional design. However, this is a tedious operation and the gloves are likely to be torn or punctured by sharp objects present in the waste. Experience at Harwell has shown that where detailed sorting is necessary it is advantageous to use operators in pressurized suits as the output is increased as is the safety.

VOLUME REDUCTION

Sorting is one method of reducing waste volume if incineration is to be used for the combustible fraction. Volume reduction may not be so important if large areas of land are available for burial of wastes. Other volume reduction methods are:

BALING AND COMPRESSION

The simplest method of volume reduction is to use a baling press and the greatest efficiency is obtained if this is hydraulically operated. The greatest potential hazard which can arise from the baling process is of inhalation and ingestion. In consequences it is good practice to extract the air from around the press and filter it before discharge.

The volume reduction obtained depends on the type of waste material but with paper, glassware, thin-walled metal tubing etc., a 6 to 1 value may be expected.

It is common practice to compress the waste material in a thin metal container. By this means the baled material retains its reduced volume.

SLIDE 3 Flowsheet for Compaction of Solid Wastes (France) (69-10570)

This slide shows a French compression system.

SHEARING, CUTTING, OR SAWING

BREAKING OR CRUSHING

Laboratory waste will always contain a high proportion of glass. A glass crusher is useful in producing a fine powder which will fill voids in containers of other waste material.

SHEREDDING

A special problem may be caused by the presence of plastic material in the waste. Certain polymers are not easily incinerated and not easily compressed. A simple shredding machine can be used which will cut the plastics and similar materials into controlled sized fragments. By this method a volume reduction of 4 to 1 may be obtained.

DISMANTLING

Large equipment items are dismantled by practically all feasible methods.

COMPACTION IN BURIAL

In certain cases, little attempt is made to reduce the volume of solid wastes prior to final disposal. In these instances it has been found to be more economical to accept a relatively small volume reduction and utilize more disposal area. In one example, solid wastes are packaged as received and transferred to a burial pit. After a layer of waste has accumulated, it is recovered with soil which is is moved by large, heavy tractors. The wastes are compressed in the operation for a volume reduction of about 30%. In other cases, weight of overburden alone provides a minor amount of volume reduction.

INCINERATION

As much of the waste arising is combustible in nature, incineration can offer a very substantial volume reduction. An incinerator suitable for radioactive waste is, however, of necessity a complicated plant requiring more than usual maintenance. The process is therefore expensive and should only be employed if it can be demonstrated that benefits will result. For example, incineration is not widely practiced in the United States because it is cheaper (capital and operating costs) to compress the solids or solidify sludges in concrete and ship them to an approved burial ground.

For waste which is completely combustible a volume reduction of between 60 and 80:1 can be obtained. On the other hand as the total solid waste arising is a mixed collection the overall volume reduction may be considerably less. The table below give details of the findings at K.A.P.L. in the United States.

Solid Waste Handling Studies at K. A. P. L.

(Volume reduction of solid waste)

	Volume as Collected (m^3)	Volume after Baling (m^3)	Volume after Incineration (m^3)
Paper, clothes, etc.	359.41	50.94	7.08
Filters	62.26	62.26	29.15
Evaporator bottoms	39.62	39.62	39.62
Miscellaneous	186.78	186.78	186.78
	648.07	339.60	262.63

Incineration has been practiced at Harwell since 1950. Today two incinerators, one dealing with 200 lb/hr and the other 400 lb/hr, are in use, and a small experimental plant is undergoing trials.

The heat of combustion of the wastes being burned is a very important consideration. This value will affect the temperature of the operation which, in turn, will determine the condition of off-gases and residue. Generally, the furnace temperature should not drop below 700°C during the operation and ordinarily should not exceed 1100°C. The upper limit is determined by the materials of construction of the incinerator.

At lower furnace operating temperatures, the amount of unburnt particles in the off-gases is greater and more difficulties with the off-gas cleaning system will ensue.

SLIDE 4 Small-Scale Incinerator Developed at Harvard Air Cleaning Laboratory (69-10571)

A small incineration plant has been designed at Harvard for use on sites which do not have liquid effluent systems. It consists of an incineration unit, a cyclone, an electrostatic precipitator and fiber filters. The incinerator has an overfire air supply which enters the combustion chamber tangentially. The advantages claimed are (1) the elimination of gas flow fluctuations as the charge burns and diminishes, (2) increase in gas stream turbulence giving rise to better mixing of combustibles and air, and (3) increased combustible gas retention time and increased solids retention in the burning chamber due to the centrifugal forces exerted on the particles.

The waste is introduced in packages through a sliding door, the bottom of which is located 15 cm above the grate. A two-pronged sliding fork, inserted through the loading door permits temporary suspension of wet packages above the grate until they are dry. The off-gases are cooled by dilution air before the cyclone. The incinerator grate can be rotated about its centerline to facilitate cleaning.

SLIDE 5 Typical Layout for Radioactive Waste Incinerator – Harwell, U. K. (69-10572)

Although this incinerator has given excellent service and is still in use, it has certain disadvantages. The furnace is made of unlined stainless steel and, as a result, the maximum temperature obtainable is too low for burning certain wastes such as animal remains. The off-gases are cleaned by a wet-scrubber and cyclone and the acidic products of combustion, particularly the chlorine compounds from P. V. C. and similar materials, caused corrosion of the metal parts. In recent years many of the problems have been overcome by using resin-glass laminates for replacement parts, pH control, better filtering of the scrubbing liquors and improving operating techniques. From hand-packed wastes as received to ash and sludge after incineration, an overall volume reduction of 66:1 is obtained.

Owing to the shortcomings of the above plant and the increasing arisings of combustible waste, another incinerator was built in 1959. The furnace is lined with refractory bricks to ensure higher burning temperatures and the plant is equipped with a "dry" filtration system. The latter consisted of woven glass fiber bags in the primary box followed by high efficiency filters in the final stage. During inactive trials volume reductions of 80:1 were obtained.

Unfortunately during the first six months of operation the burden on the primary bag filters caught fire on three separate occasions. This resulted in the desintegration of the filter material but the debris was held by the final filters. Owing to the cost of filter renewals it was decided to abandon the dry system for the time being and the exhaust ducting was connected to the wet scrubbing system of the older plant.

GAS CLEANING

An extremely important consideration in the design of an incinerator for radioactive wastes is the clean-up of exhaust gases. The radioactivity associated with particulate matter in the gas must be prevented from contaminating the environment. The problem is difficult because the gases are hot (about 800°C at the exit of the combustion chambers) and a very high degree of cleaning, such as that provided by absolute filters, is necessary. Two general methods are used – the wet method or the dry method. In either case, the gas must first be cooled. This can be accomplished by dilution with outside air, quenching with water in a column or scrubber, or by passing the gas through air or water cooled heat exchangers. Each of these methods has certain disadvantages. When dilution air is used, the quantity of gas for further cleaning is appreciably increased and the equipment necessary must be sized on the basis of the sum of the volumes of gas and dilution air. The quenching operation absorbs acids from the gases but, though quench water may be recirculated, a significant amount of contaminated liquid waste results. With the heat exchangers, condensing gases cause severe corrosion problems. The method selected for cooling is based on a study of all factors – type of waste, types of gases emitted, type of radioactivity, availability of facilities for treating liquid waste, etc.

Following cooling, the wet method of gas cleaning would include a venturi scrubber, a wet cyclone or perhaps a cleaning column with ceramic spheres, Rasching rings, or similar materials. The water used would usually be recirculated and treated for particle removal, temperature control and pH adjustment. If further treatment of the gas is required, electrostatic precipitators or absolute filters can be used. If the absolute filters are required, the gas must be treated for moisture, removal of which can be accomplished by heating it above the dew point. Oftentimes, prefilters are placed ahead of the absolute filters to extend their useful operating life.

In the dry method of gas cleaning, cooling is usually followed by cyclone separators for removal of the larger particulates. The cyclone effluent is then treated through bag filters or electrostatic precipitators. The bags should be of fiberglass of similar contruction with some fire resistance. In the final stage, the gas is cleaned by absolute filters ordinarily protected by pre-filters.

The systems described above are two very general methods. Incinerators in operation today use similar arrangements and various combinations. Improper design of the cleaning system can result in very high operating costs and therefore a careful study should be made before final decisions are reached. A well-designed system can provide decontamination factors in excess of 10^5.

GROUND DISPOSAL

Ground disposal operations have taken many forms depending upon availability of land, elevation of the ground water table, amount of rainfall, direction of ground water flow, ground water use in the area, geologic formations, philosophy regarding future recovery, etc.

In some cases, the disposal might be more correctly considered as semi-permanent storage. Particular types of wastes are packaged and placed in abandoned mines, tunnels, fortifications, etc. Complete records are maintained so that specific items can eventually be recovered. Salt mines are being used in this manner for storage of low to intermediate level solid wastes in a number of countries and have been studied for disposal of high-level wastes.

SLIDE 6 Schematic Cross-Section of Burial Area (68-11890)

This slide shows a compressed scale diagram of the geology at Oak Ridge. This is a high rainfall area and can be used to illustrate several principals. The dark shaded area is the permeable zone and the shale is largely impermeable. Ideally a burial ground would be located on the top of the center hill, high above the water table, and should be covered over with concrete or asphalt to limit the amount of water entering the burial pit. If the ground is permeable, any water entering the pit passes through. In some areas, such as Oak Ridge, the earth tightly sorbs many of the nuclides present (Cs, Sr, but not ^{3}**H** or Ru). Other sandy areas, such as at Savannah River, have lower sorption capacity.

SLIDE 7 Poor Placement of Burial Pit (65-8768)

This slide shows a poor placement of a burial pit. Any water entering the pit is retained by the low permeable shale. The pit should be located high up where the land slope is less.

SLIDE 8 No Title (Photo 47476-C)

This illustrates the retention of water in an open pit in an impermeable area.

SLIDE 9 No Title (Photo 45989)

This slide shows drums of waste stacked in an experimental pit at Oak Ridge.

SLIDE 10 No Title (Photo 46348)

This slide shows the asphalt cover over the experimental pit. The asphalt cover reduces but does not eliminate water seepage into the pit.

SLIDE 11 No Title (Photo 45993)

Recommendations have been made by T. F. Lomenick for solid burial at ORNL, a high rainfall area where, in general, weathered shales and interbedded silty limestone underlie the burial area. The pit should be prepared as shown in this slide to reduce infiltration and to monitor rain water that does find its way into the trenches and leaches the solids after they have been covered. As seen, the bottom of the trench is sloped toward on asphalt-lined sump containing a 6-in.-diam perforated casing from which samples can be withdrawn from the surface. (The casing may also serve as a permanent marker for the trench.) After the trench is filled to within a foot or two of the surface, it is mounded with shale for about 3 ft and tightly packed to allow rainfall to drain rapidly off.

Because the trench lenght is an important consideration in catchment area seeps, especially where trenches are excavated in sloping surfaces, it is necessary to restrict trench lenght. Although the length will depend on the topographic slope, it is recommended that they not exceed 100 ft. A 10-ft-wide trench appears to be adequate, and a 5-ft spacing between trenches should allow reasonable working room and also insure the integrity of the holes.

In order to suspend waste within the proposed burial site above the water table, and thus prevent its continuous leaching by circulating ground water, the critical depth-to-water-table contour map should be closely followed during trench excavations. By allowing a spacing of at least 1 ft between the bottom of the trenches and the water table, the depth of burial between the 6-ft and 11-ft contours is limited to 5 ft. Similarly, the depth of burial between the 11-ft and 16-ft contours and the 16-ft and 21-ft contours is restricted to 15 and 20 ft, respectively. In general, the shales and interbedded silty limestone that underlie the burial site are weathered, and thus easily excavated by power equipment, to depths ranging from 20 ft or more on the summits of the hills to depths of 5 ft or less in the valley floors. Since the detph of weathering corresponds roughly to the limits of burial depth imposed by ground water, there should be little difficulty in excavating trenches by backhoe, bulldozer, or drag pans to the depths suggested in the critical depth-to-water-table contour map. In some places resistant limestone lenses up to several inches in thickness occur within a few feet of the land surface and will therefore limit the depth of auger hole burials and perhaps even trench excavations.

SLIDE 12 Burial Authorization for Radioactive Contaminated Solid Waste (69-11040)

Shows one of the forms used at ORNL. It is the authorization required before waste is collected from the research facilities for transportation to the storage area. The customer must execute that portion of the form reserved for his use to pass on pertinent information for handling the contents. He is assisted by his Health Physics surveyor who is familiar with his operations and his facilities. Our field supervision confers with the sender before any of our people become engaged in the particular operation.

SLIDE 13 Burial Ground IMB Computer Log (69-11039)

This slide shows a data card which is used to put a Burial Ground log on the IBM computer. It gives thedate, the building from which the waste is generated, the badge number of the person authorizing the disposal, the location of the waste in the trench or well, and it provides a place for the quantity of waste involved in this shipment. For off-area shippers, the bill of lading is shown.

A monthly summation is provided by the IMB machine. Each site using the ORNL burial area is given a number. We have been required to re-enter the trenches on eight occasions in order to recover an item from storage. With this IBM log we are able to pinpoint the item in the field. If we know the date of burial, point of origin or the person authorizing the burial, we're well on the way in determining the actual location of the item. History of adjacent burials are evaluated to determine type and levels of radiation that are to be encountered while digging.

SLIDE 14 No Title (Photo 97216)

This slide shows the container being delivered to the disposal site. The container is set aside and covered with a sheet metal rain cover until such time as it is economical or proper to make the disposal. I say proper, because these burials have to be made under "no wind" conditions. These rain covers are of light sheet metal and are easily handled by two men. We have four Dumpster pans which are lead lined. Two are lined with one inch of lead and two are lined with two inches of lead. The design was governed by the lifting capacity of our hoist truck. The yellow container which you see to the left of the five units is a conventional Dumpster pan from our TRU facilities, about which I'll say more later. When we have accumulated sufficient number, the rigging crew is scheduled and the dumps are made.

SLIDE 15 No Title (Photo 97217)

The next slide shows an actual disposal operation. The men are dressed out in coveralls, air masks, and shoe covers. This particular crane is a 35-ton motor crane, but we also have other cranes which we use. We use whichever is available. The container about to be lifted is a one-inch, lead-lined container. It is waterlight, has hinged covers, and is loaded and emptied from the top. The yellow container on the right of the picture is a conventional 4-cubic-yard watertight Dempster Dumpster pan. It is unlined.

SLIDE 16 No Title (Photo 97215)

This slide shows waste casks from the ORNL Transuranium Facility (TRU) in the burial trench. Wastes from TRU at ORNL contain significant amounts of α, β, and γ-emitting nuclides. There is a packaging cell in which the waste is incapsulated in plastic containers and sealed. The waste is then placed in a plastic lined, disposable concrete cask. We have two versions of these casks. A 6-in. wall 6000 lb and a 12-in. wall 12,000 lb unit. Both are 7 feet tall and 48 in. outside diameter. They can accommodate a ton of waste. When the cask is full the plastic liner is sealed, the cask is covered, sealed and banded with stainless steel shipping bands. The cask is moved to the burial site by truck, lowered into a trench and covered with concrete.

SLIDE 17 Concrete Trench at Chalk River (Photo 97218)

At Chalk River, Canada, the ground water is 2 to 4 m below the surface and concrete trenches or concrete pipes are used to bury waste. This slide shows a concrete trench. The trenches are long and narrow and divided into 6 to 10 sections, one section at a time being used. Each section is approximately 7 m long. When a section is being used it is fitted with a temporary plywood roof which can easily be removed. The remaining sections of the trench are left open to the weather and are pumped out just before use. When one section is nearly full sand is put on top of the contents and a concrete roof poured over the whole. A metre of soil is put over the concrete roof. The trenches are usually about 2 m wide and 2-1/2 m deep. Vertical shafts of concrete pipe set in a concrete pad are also used. The exterior of the column is covered with asphalt and when the column is full, it is capped with concrete.

Concrete monoliths are used for medium-activity wastes (approximately 5 μc/ml) of mixed fission products in 2.5 N HNO_3. The solution is mixed with cement in 200-liter steel drums. Bentonite (2 wt %) is added to retain excess liquid. Forms are built around the stacked drums and concrete is poured around and on top of the drums forming a solid concrete block 1-1/2 m below the ground. No significant leaching has occurred during nine years from this type of operation.

SLIDE 18 Excavation at Los Alamos for Solid Waste Burial (Photo 97219)

At some sites, elevation of the ground water table creates no problems and rainfall is very low. At Los Alamos, ground water is very deep. The water table is 300 m below ground but perched lenses can be found 60 to 240 m below the surface. Very large pits are excavated and filled with alternate layers of solid waste and soil covering. A log is maintained on the date and location in the pit of all wastes. to permit recovery if necessary. The principal contaminant of the wastes is ^{239}Pu which laboratory tests have shown will not measurably migrate through the volcanic tuff type soil.

SLIDE 19 Waste in Pit at Los Alamos (Photo 97221)

SEA DISPOSAL

At the present time there are no international regulations which have been promulgated for control of the disposal of solid radioactive wastes to the seas. The IAEA is vitally interested in this method of disposal and has an increasingly expanding programm designed to eventually develop internationally accepted regulatory measures. Agency panels have met to advise the Director General on recommended procedures and programmes to achieve international agreement and Agency symposia have provided scientists with the opportunity to discuss all related problems. At the present time, the Agency is encouraging all Member States to report disposals to the seas so that an international record may be maintained.

National attitudes toward disposal of radioactive wastes to the seas vary from complete opposition to disposal of any radioactive wastes to complete acceptance for disposal of wastes of low and intermediate levels.

Sea disposal practiced to this time has been largely on the basis of no future recovery. In most cases, site requirements have been similar to the following:

1. Must be an area not used for bottom fishing. Areas where depths exceed 2000 m are usually chosen.
2. Should be little likelihood that containers will move outside the designated area. Adequate package density and lack of bottom currents in the area will usually satisfy this requirement.
3. There should be no undersea cables in the area.
4. Currents in the area should be parallel to or preferably away from the shore.
5. There should be a minimum of mixing between deep and surface water.
6. Strong surface currents enhance dilution of any activity released from the containers.
7. The area should be away from recognized shipping lanes and be at least 50 nautical miles from the nearest shore or edge of the nearest continental shelf.

These requirements cannot always be met completely and minor adjustments are often necessary. In any case, before a dumping operation is undertaken, a hazard assessment, based on the above criteria, must be made. The assessment takes into account all aspects of the planned operation including type of packaging; estimate of life of the package exterior; marine plants and organisms in the area; uptake of radionuclides by such organism; transport, sedimentation, sorption and diffusion processes; the critical pathway to man based on diet studies; and a number of other factors. Even though not all contributing factors are completely understood, it is believed by many that a very careful step by step assessment, with conservative assumptions were required, will permit a determination of the amount of radioactive material which can be discharged to an area without causing any injury to man or to the overall population of marine organisms.

Containers used in the actual operation must be designed to meet certain requirements. They must be of dense material strong enough to ensure safe handling and transport and to survive the impact with the sea surface and bottom. A common design consists of a reinforced concrete shell in a steel drum. To ensure that the containers will sink, it is normal to require that package density exceed 1.2. The package should contain no voids and a minimum of compressible material so that it will not rupture under the pressure which increases one atmosphere for each 10 meters of depth.

Sea disposal has been practiced by a number of countries and no evidence of the waste nuclides has been found in monitoring operations to date. It is hoped that international agreements on such operations can be reached in the near future to assure all that safe use is made of international waters.

REFERENCES AND EXCERPTS FROM:

1. *Technology of Radioactive Waste Management Avoiding Environmental Disposal*, Technical Reports Series Nº 27, IAEA, Vienna, 1964.

2. L. A. Emelity, "Treatment and Disposal of Radioactive Solid Wastes." IAEA Regional Training Course on Radioactive Waste Management, Rio de Janeiro, Brazil (October 14-25, 1968).

3. R. H. Burns, "Solid Waste Treatment," Inter-Regional Advanced Training Seminar on Radioactive Waste Management, Tokai-Mura, Japan, October 4-15, 1965.

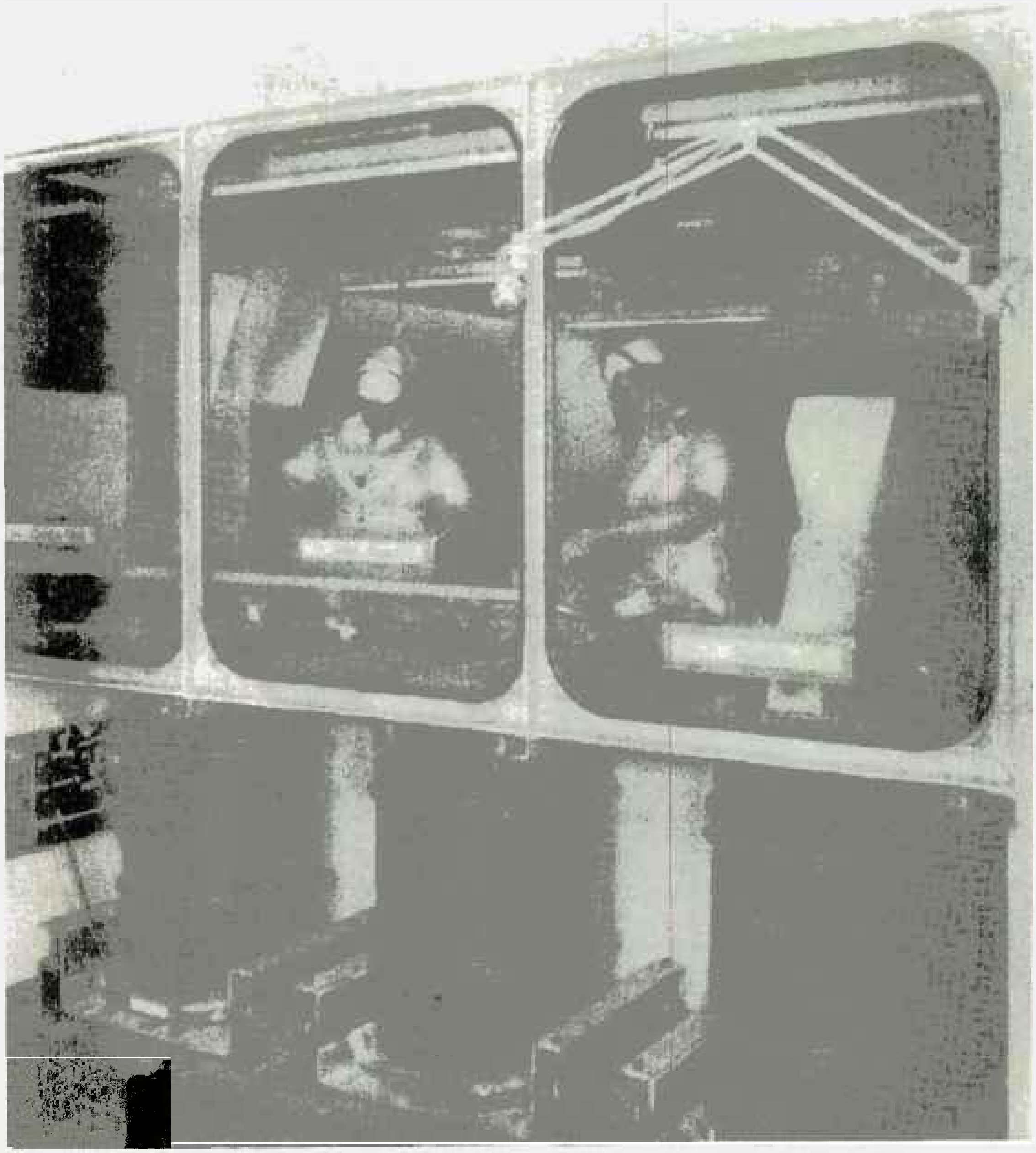
4. T. F. Lomenick and H. J. Wyrick, *Geohydrological Evaluation of Solid Waste Storage Area 6,* ORNL-TM-1327 (December 1965).

5. T. F. Lomenick and K. E. Cowser, "Land Burial of Solid Waste at Oak Ridge National Laboratory," Ground Disposal of Radioactive Wastes, Second Conference Proceedings Held at Atomic Energy of Canada Limited, Chalk River, Canada, September 26-29, 1961, TID-7628 (March 1962).

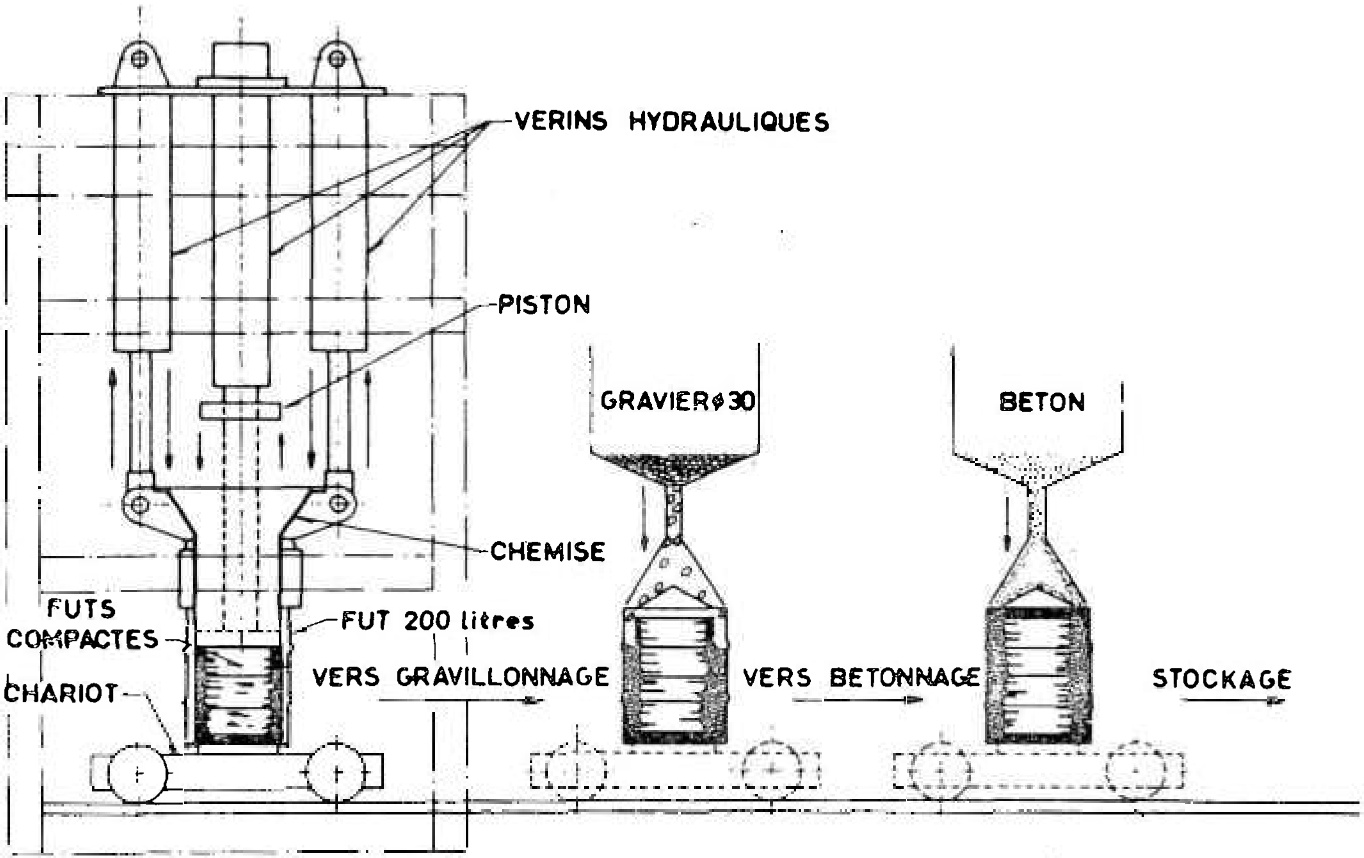
6. *IAEA Practices in the Treatment of Low- and Intermediate-Level Radioactive Wastes,* Proceedings of a Symposium held in Vienna, December 6-10, 1965.

TYPES OF SOLID WASTES

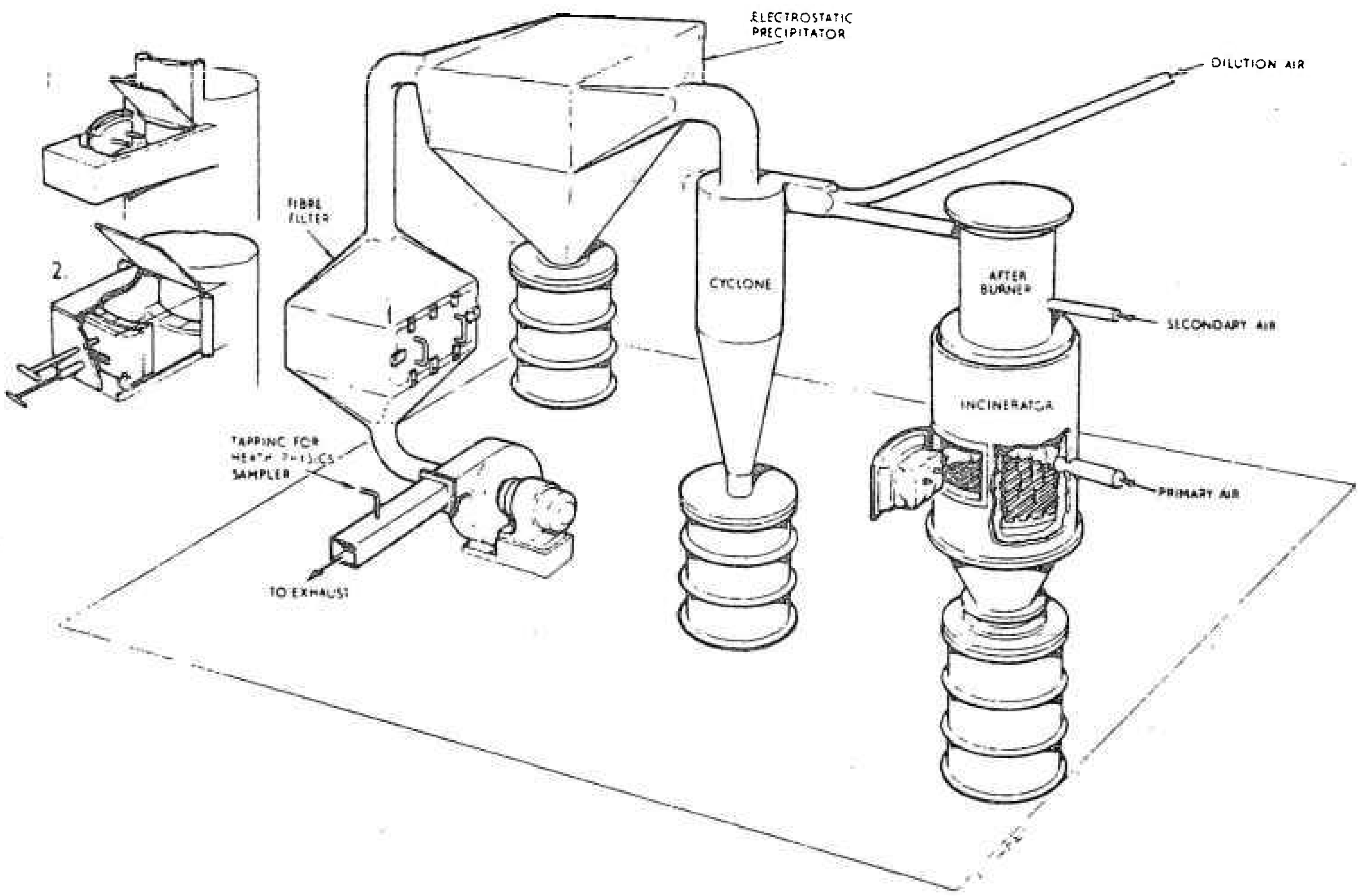
PAPER, RAGS, FILTERS
COVERALLS, RUBBER OR CLOTH GLOVES, SHOES, BOOTS
WOOD FLOORING, BENCHES, ETC.
GLASSWARE, METAL LABORATORY EQUIPMENT
PIPING, PUMPS, MISCELLANEOUS EQUIPMENT
BIOLOGICAL MATERIALS AS ANIMAL CARCASSES, VEGETATION, ETC.
CHEMICAL SLUDGES
EVAPORATOR CONCENTRATES
ION EXCHANGE RESINS
PLASTIC MATERIALS OF ALL KINDS



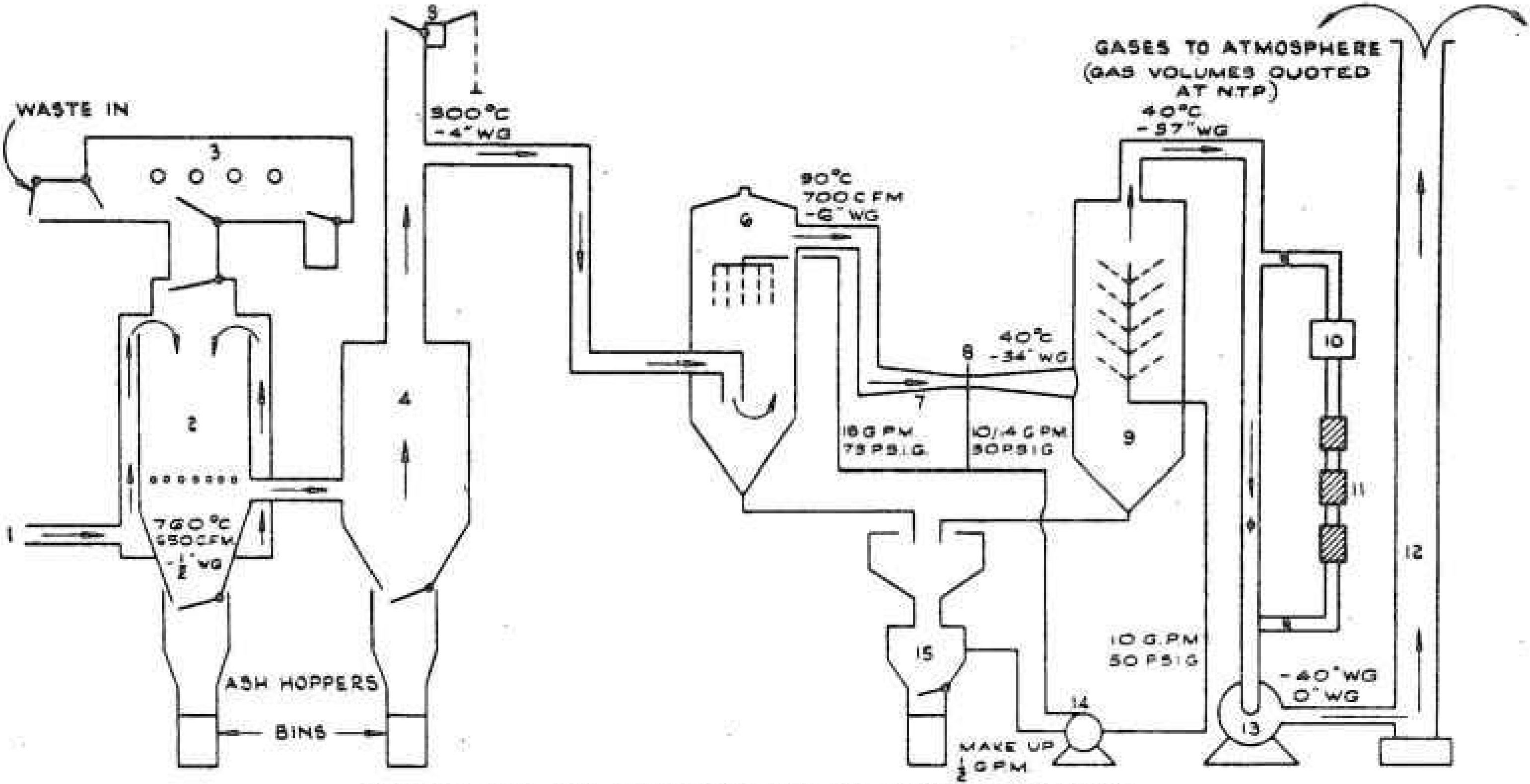
SORTING OPERATIONS IN SEALED AREA AT HARWELL



FLOWSHEET FOR COMPACTION OF SOLID WASTES (FRANCE)



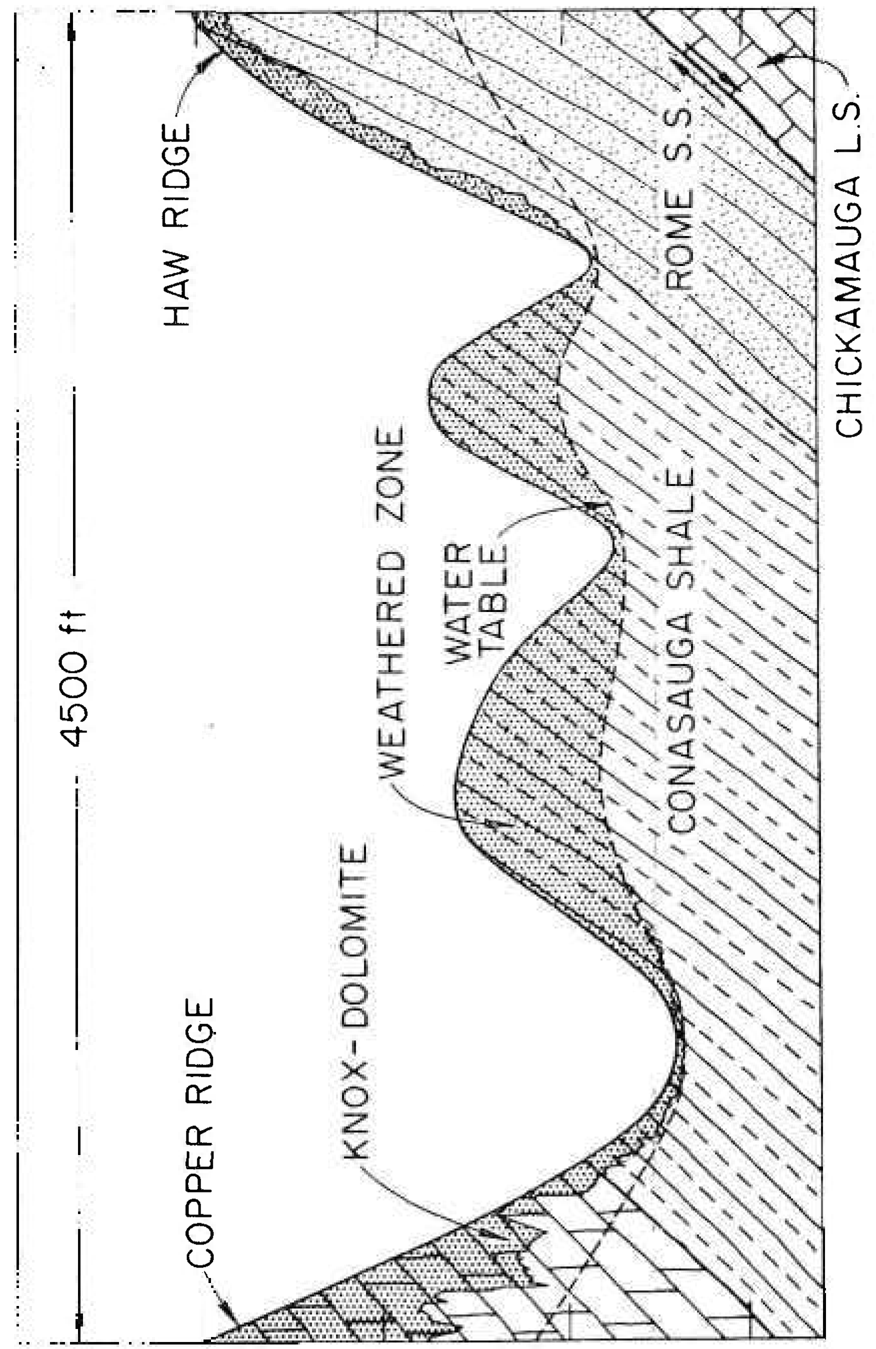
SMALL-SCALE INCINERATOR DEVELOPED AT HARVARD AIR-CLEANING LABORATORY

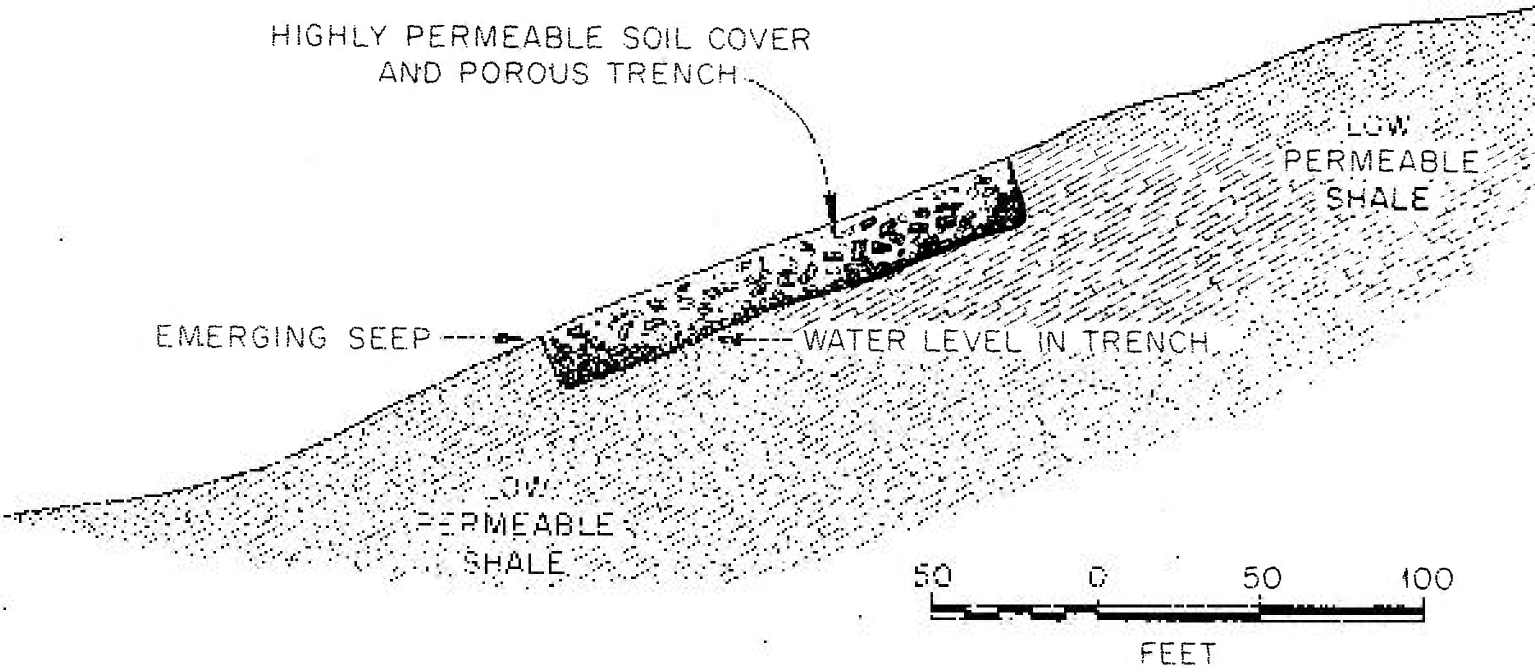


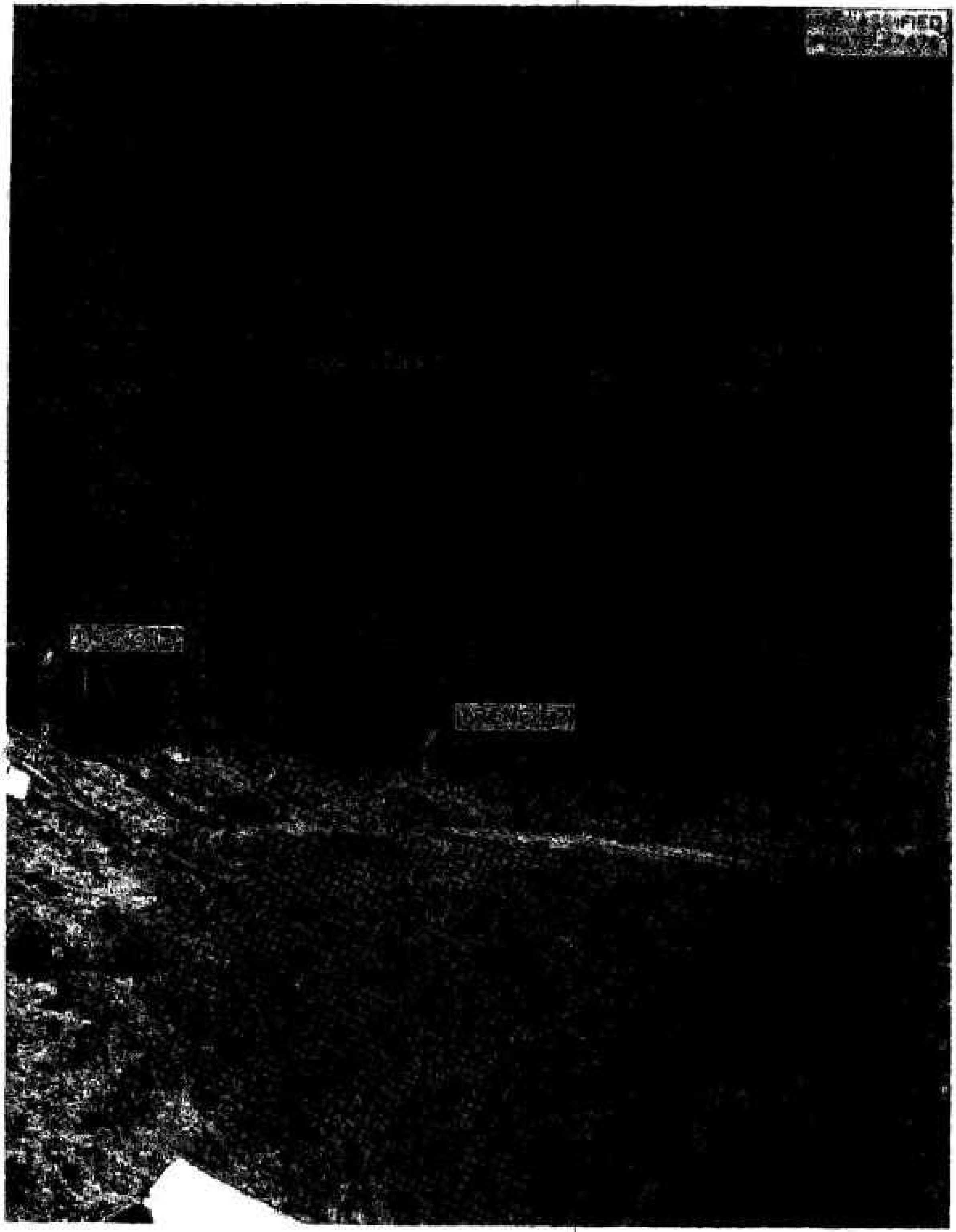
TYPICAL LAY OUT FOR RADIO ACTIVE WASTE INCINERATOR

1. AIR INTAKE
2. INCINERATOR
3. SORTING CABINET
4. FLY ASH SETTLER
5. SAFETY FLAP VALVE
6. ADIABATIC COOLER
7. VENTURI SCRUBBER
8. THROAT WATER JETS
9. CYCLONE SCRUBBER
10. GAS HEATER
11. FILTERS
12. DISCHARGE STACK
13. FAN
14. RECIRCULATION PUMP
15. FILTER

TYPICAL LAYOUT FOR RADIOACTIVE WASTE INCINERATOR


ELEVATION (ft)
950
900
850
800
750
4500 ft
COPPER RIDGE
KNOX-DOLOMITE
WEATHERED ZONE
WATER TABLE
CONASAUGA SHALE
HAW RIDGE
ROME S.S.
CHICKAMAUGA L.S.


HIGHLY PERMEABLE SOIL COVER AND POROUS TRENCH
LOW PERMEABLE SHALE
EMERGING SEEP
WATER LEVEL IN TRENCH
LOW PERMEABLE SHALE
50
0
50
100
FEET



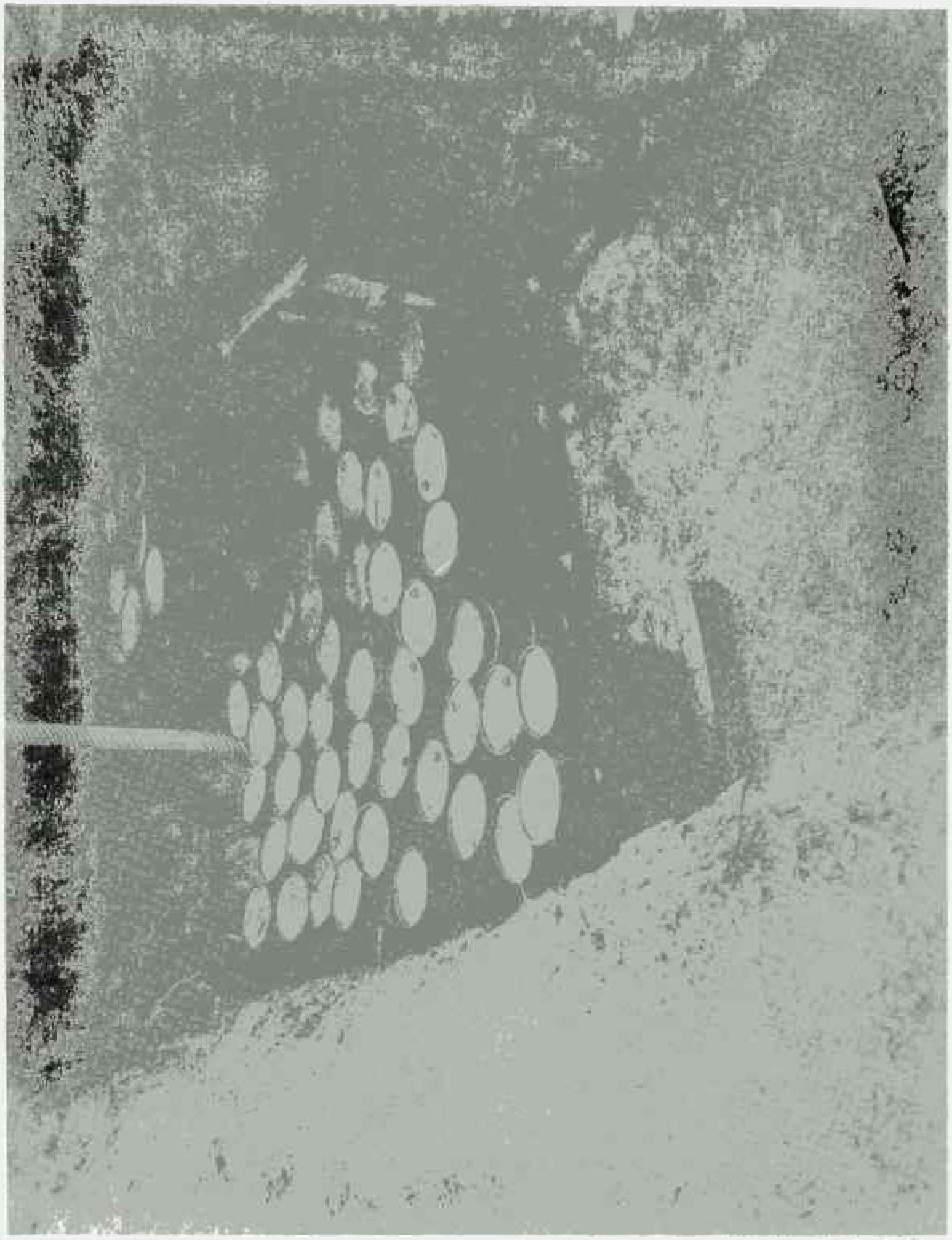


PHOTO 3993

GRAVEL UNDERDRAIN SYSTEM AND COLLECTING SUMP FOR SPECIAL TRENCH

BURIAL AUTHORIZATION FOR RADIOACTIVE-CONTAMINATED SOLID WASTE AT ORNL

REQUESTER: EXECUTE THIS SECTION BEFORE ARRANGING MATERIAL TRANSFER

THE FOLLOWING MATERIALS ARE TO BE BURIED

ORIGIN-BLDG	SECTION OF BLDG.	TYPE OF CONTAINER	PRINCIPLE RADIOACTIVE ISOTOPES PRESENT

PROTECTIVE CLOTHING REQUIRED FOR BOTH TRANSPORTATION AND BURIAL (BE SPECIFIC)

PRECAUTIONS: HEALTH PHYSICIST MUST: ☐ ACCOMPANY SHIPMENT TRANSFER ☐ BE PRESENT AT BURIAL

☐ OTHER

BURIAL INSTRUCTIONS *(See HPP-32, Responsibilities, 1.0 Area Supervision)*

TELEPHONE BURIAL GROUND FOREMAN PRIOR TO MATERIAL TRANSFER (EXTENSION 6356 OR 6046)

REQUESTER'S AUTHORIZATION FOR DISPOSING MATERIALS	NAME		BADGE NUMBER	BUILDING
	DATE	DIVISION	DEPARTMENT	ACCOUNT CHARGE

HEALTH PHYSICS: COMPLETED AT POINT OF ORIGIN OF SOLID WASTE AND BEFORE TRANSFER OF MATERIAL TO BURIAL GROUND

UNUSUAL HAZARDS

☐ **CAUTION:** DO NOT TEAR OR DAMAGE PACKAGING! ☐ **CAUTION:** FACE MASKS MUST BE USED DURING DUMPING OPERATIONS!

☐ OTHER

RADIATION LEVEL

BETA-GAMMA-SHIELDED, mrem @ inches; UNSHIELDED, mrem @ inches

SURFACE CONTAMINATION- d/minute Bδ d/minute Alpha

PRECAUTIONARY MEASURES TO BE OBSERVED

HEALTH PHYSICS APPROVAL FOR MATERIAL TRANSFER TO BURIAL	NAME	DATE

BURIAL GROUND: COMPLETED BEFORE RETURNING COPY TO ORIGINATOR

ALL INSTRUCTIONS NOTED WERE CARRIED OUT: ☐ YES ☐ NO ☐ SEE BELOW

UNUSUAL OCCURRENCES OBSERVED

COMMENTS REGARDING FIELD WORK

BURIAL GROUND SUPERVISOR'S RECEIPT OF MATERIALS	NAME	BADGE NUMBER	DATE	TIME

DISTRIBUTION: Original - Burial Ground Foreman
1st Copy - Returns Completed to Originator
2nd Copy - Retained by Originator

UCN-[illegible]
[illegible]

BURIAL GROUND LOG

OAK RIDGE NATIONAL LABORATORY

ORIG. SITE NO. 1 – 5

BUILDING NO. 6

PICKUP [illegible] NO. 12

AUTHORIZED BY (BADGE NO.) 15

BILL OF LADING 20 – 29

TRANSPORTATION
RAIL = 1
TRUCK = 2
RIGGER = 3
30 ☐

ALPHA ACTIVITY
HIGH = 1
MED. = 2
LOW = 3
31 ☐

BETA-GAMMA ACTIVITY
HIGH = 1
MED. = 2
LOW = 3
32 ☐

HANDLING
STANDARD = 1
SPECIAL = 2
S.S. MATERIAL = 3
OFF-AREA = 4
33 ☐

BURIAL GROUND 34

BURIAL DATE

YR. 36 37: 6 6

MO. 38 39

DAY 40 41

LOCATION

TRENCH NO. 42

WELL NO. 46

FEET FROM ZERO 50

FEET FROM BOTTOM 53

BURIED BY (BADGE NO.) 55

KEYPUNCH NOTE: RIGHT ADJUST DATA IN FOLLOWING FIELDS.

COMB'STLE CU. FT. → 62

MELTABLE CU. FT. → 65

NON-COMB. CU. FT. → 68

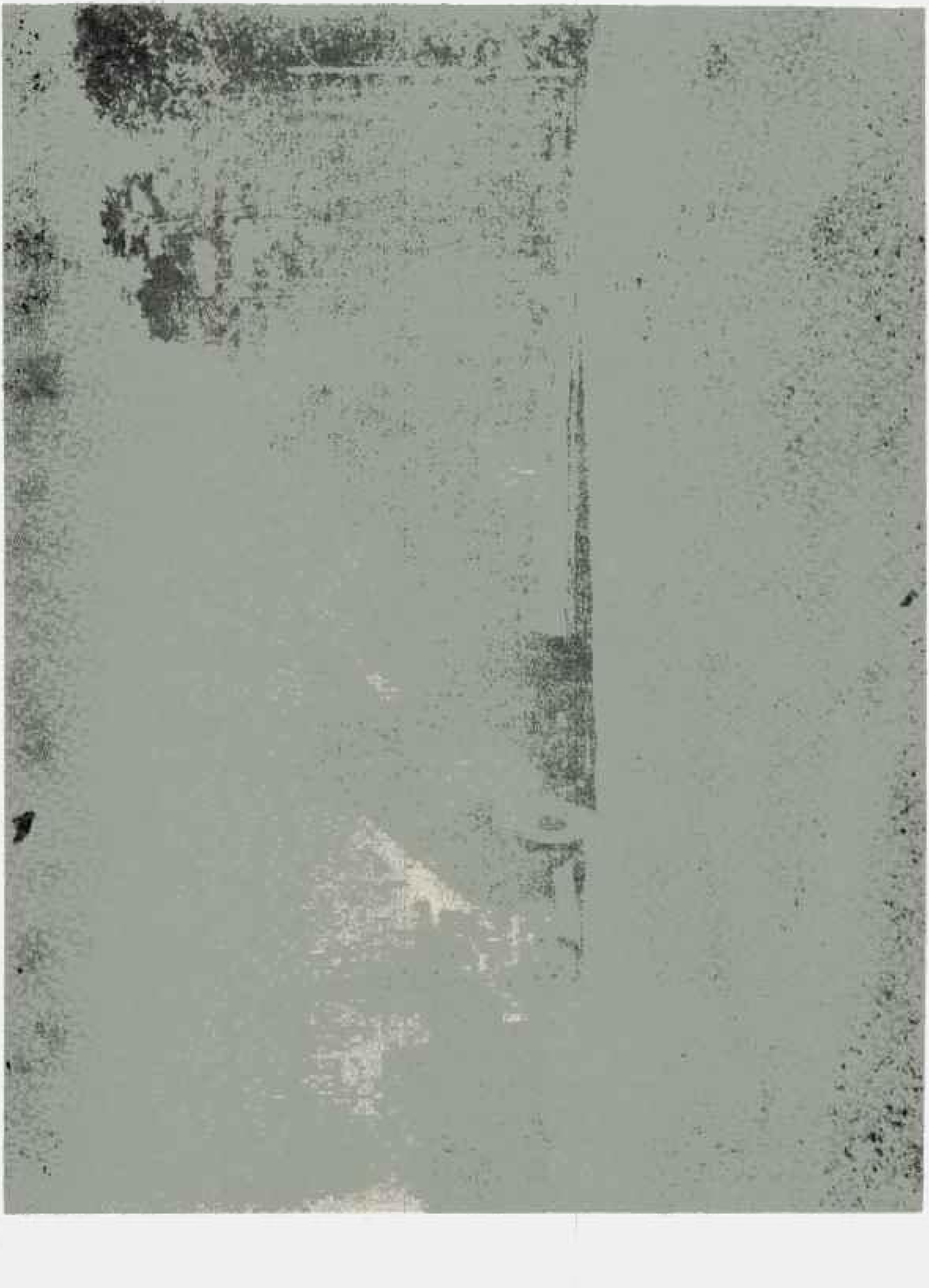
SLUDGE GALS. → 72

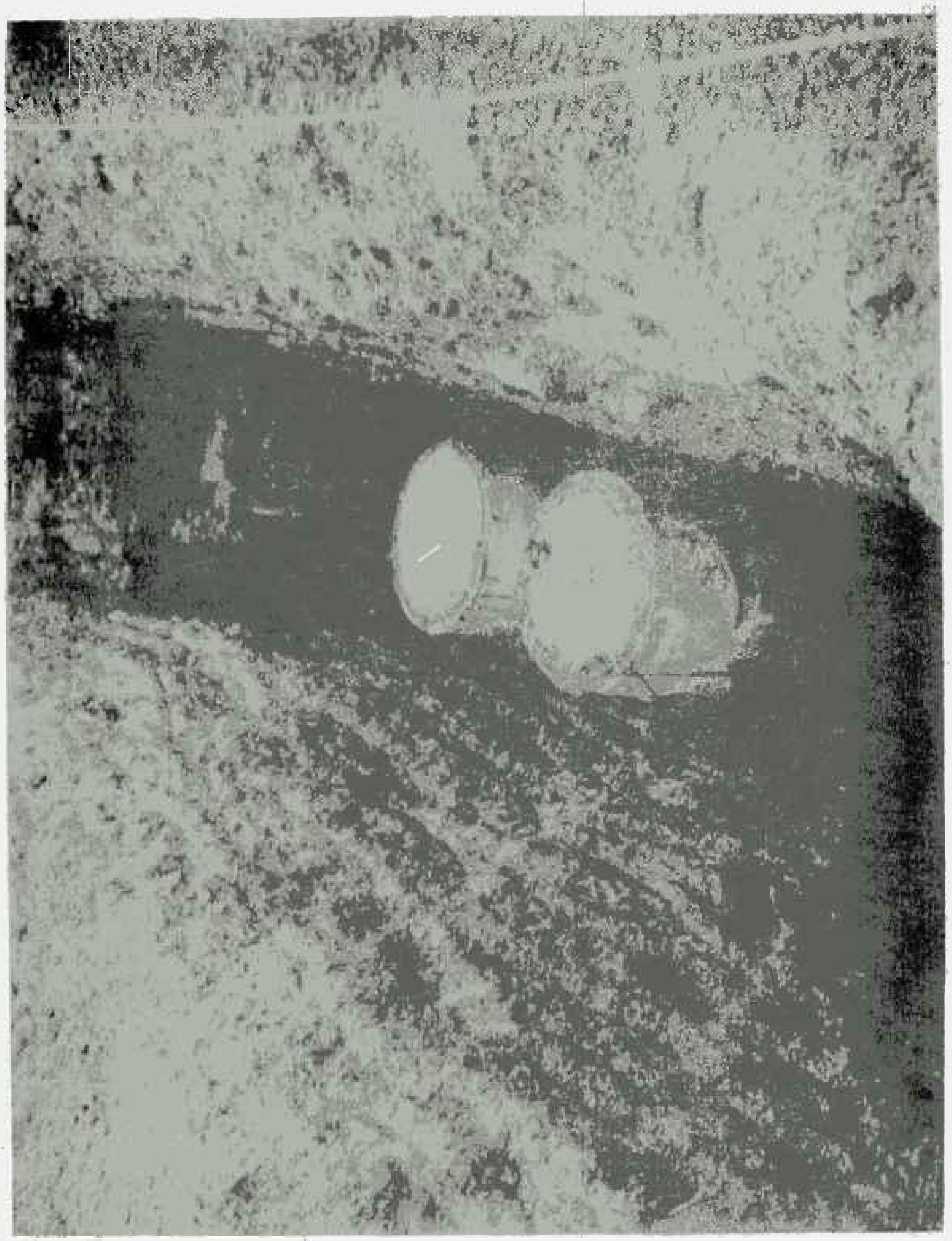
OFF AREA CU. FT. → 76

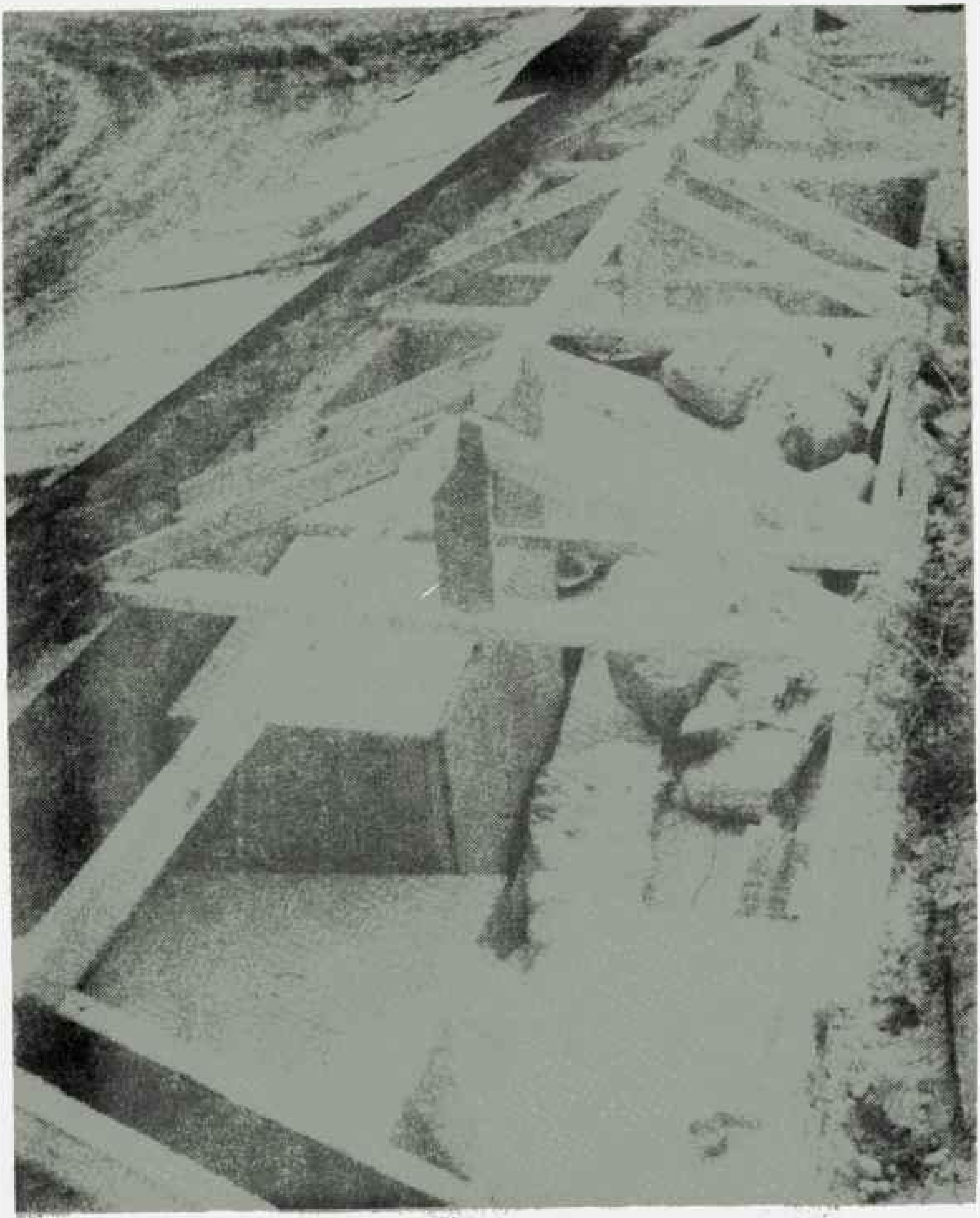
77

PER LOC. REQUIRED → 80

UCN-3549
(38 5-67)

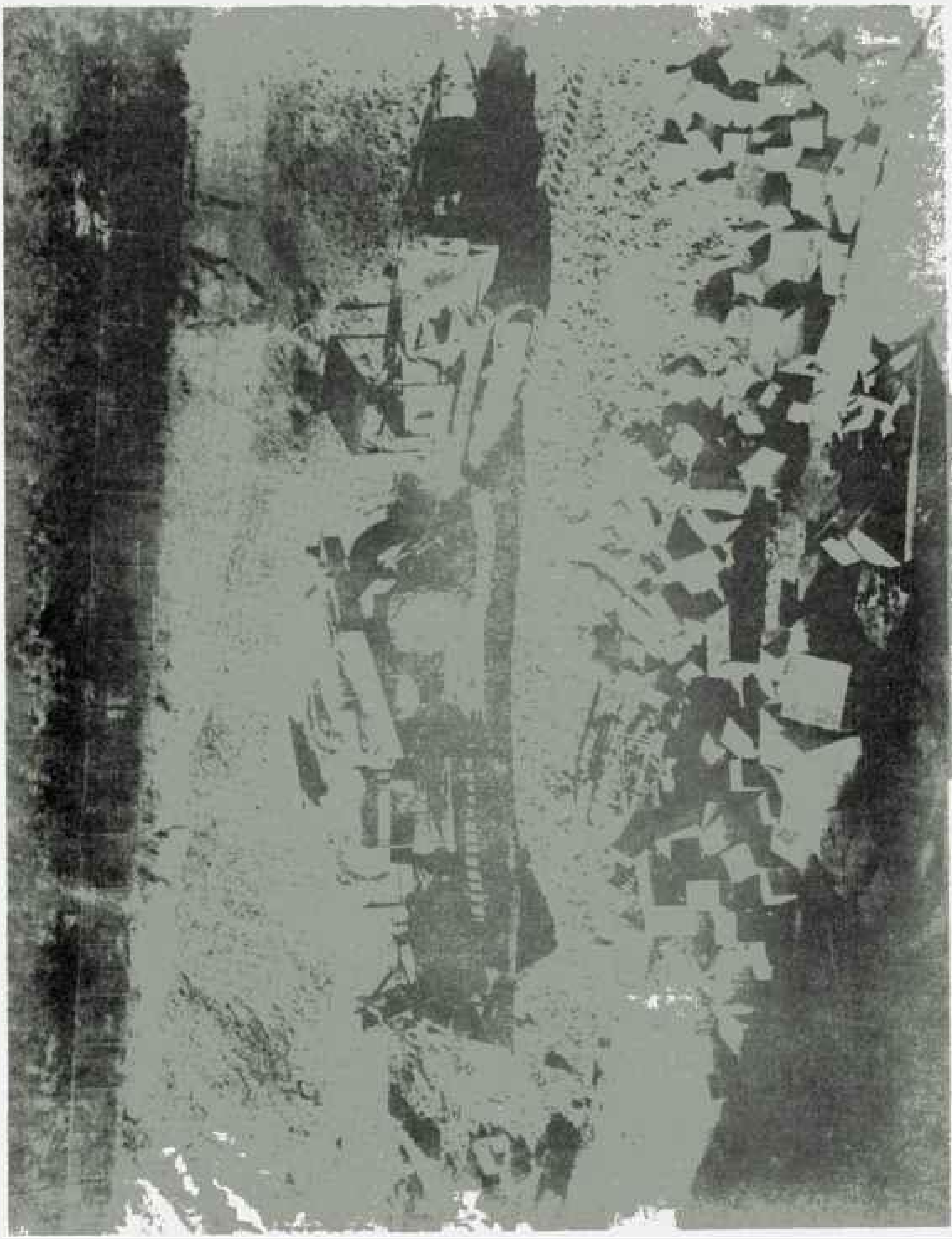






CONCRETE TRENCH AT CHALK RIVER

EXCAVATION AT LOS ALAMOS FOR SOLID WASTE BURIAL



WASTE IN PIT AT LOS ALAMOS

DISPOSAL OF LOW AND INTERMEDIATE WASTES INTO THE EARTH BY HYDROFRACTURING

R. E. Blanco

The development of the hydrofracturing method for injection of low- and intermediate-level waste-cement slurries into the earth has proceeded since about 1960. Experimental injections were made at ORNL in the period 1964 to 1965. The method was accepted as the routine disposal method for waste concentrates in December 1965. Since that time, six injections have been made with volumes varying from 60,000 to 120,000 gal, a total of 890,000 gal, and containing a total of about 330,000 curies. This includes about 540,000 gal of waste, 114,000 gal of water, and 236 gal of cement. Injections can be made at 700 to 1000 ft below the surface but most injections have been at approximately 840 to 870 ft. The cement grout spreads out in a thin layer, about 2 to 8 mm thick.

The method is designed to inject wastes far below the water level into formations where future contact with water is unlikely. The circulating water level at ORNL is limited to about 200 ft under the surface. The method has proven successful at ORNL and research is now being conducted to determine the feasibility of hydrofracturing in western New York State.

I have reproduced lecture notes (*) by Dr. W. de Laguna (ORNL) as a guide for this lecture. Dr. de Laguna was a principal party in the development of this method. I will also show a movie on hydrofracturing which is available at ORNL.

WASTE DISPOSAL BY HYDRAULIC FRACTURING (**)

Wallace de Laguna (ORNL)

(Figure 1) The use of hydraulic fracturing for waste disposal is an outgrowth of the use of hydraulic fracturing to stimulate the flow of oil wells. One technique for the construction of an oil well consists in first drilling a hole from the surface down through the reservoir formation, which is commonly a sandstone. A steel casing is then lowered into the hole almost to the bottom. Next, a water-cement slurry is pumped directly down the casing until the annular space between the casing and the wall of the hole is nearly filled. Then a rubber plug is put into the casing and pumped down with water until it seats on a shoulder at the bottom of the casing; Figure 1 shows this plug being pumped down. When the cement has set the well consists of the steel casing, filled with water, and tightly cemented into the rock down to and through the reservoir formation, but without any access to the reservoir.

(Figure 2) A heavy steel tubing with a small side jet near the bottom is then lowered inside the casing until the jet is opposite the reservoir formation. A slurry of water and sand under very high

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(*) This does not represent an official publication by ORNL.

(**) Informal lecture notes for paper presented at AIChe Meeting Portland, Oregan, U.S.A., Aug 1969.

pressure (3500 psi) is then pumped down the tubing while it is slowly rotated. The jet cuts a slot through the casing, the cement, and out into the reservoir rock, after which the tubing is removed from the well. The high-pressure pump is then connected directly to the well casing and pressure applied until the rock fractures at the slot. The fracturing fluid is generally oil or an oil-sand slurry.

An alternative procedure is to first drill the well only to the top of the reservoir rock, cement in casing to this depth, and then drill through the rubber plug to the bottom of the reservoir rock, leaving this section of the well uncased. When high pressure is then applied to the well, the reservoir rock will fracture at its weakest point; but as the hole in the rock is unprotected by casing, the pressure tends to enlarge the radius of the well and the fracture may well be vertical. Confining the fracturing pressure with casing, except for the slot cut with the sand-water jet, tends to promote the formation of a horizontal fracture.

(Figure 3) When the reservoir rock has once fractured, the pumping pressure drops somewhat and the pumping rate may be materially increased. In this way a considerable volume of an oil-sand slurry may be pumped down the well and out into the fracture as it is extended. As the fracture is driven farther out from the well its surface area increases, and although the reservoir rock typically has a relatively low permeability, a point will be reached where the oil is leaking off into the wall rock as rapidly as it is being pumped down the well. This point will limit the dimensions of the fracture which may be formed.

When the fracture has been extended as far as possible, the pressure is relieved and the well pumped. The fracture tried to close but is prevented from doing so by the sand, and the resulting sand-filled fracture provides a permeable pathway for the easy movement of oil out of the reservoir rock into the well.

The oil that leaks out of the fracture increases the static fluid pressure in the rock, a pressure that is exerted equally in all directions. The direction in which the fracture will extend is determined by the existing stresses in the rock, for the fracture will develop most easily normal to the least confining pressure. However, if the liquid is contained within the fracture, virtually all the force will be applied to the walls of the fracture, and the fracture will tend to extend in the direction in which it was initiated. If this direction is parallel to the bedding in a platy rock-like shale, the very small amounts of fluid that leak out between the bedding planes ahead of the actual fracture will exert a powerful influence to keep the fracture parallel to the bedding. For this reason, particularly in the early development of a fracture, a slow injection rate will aid in the extension of the fracture parallel to the bedding.

(Figure 4) For waste disposal by hydraulic fracturing, the well would be installed and slotted in much the same way, except that there would be good reason not to fracture an uncased section of well as horizontal fractures are required. The well would not be terminated in or near a permeable formation, even one of low permeability, but would have the bottom section in shale or similar well-bedded nearly impermeable rock.

The well would be slotted in the same way as an oil well, and the fracture would be initiated with water. Once flow into the well and the fracture was assured, the pump would be switched to a mixture of waste and Portland cement. This mixture would harden in the fracture which it had formed and would be isolated by the over and underlying essentially impermeable shale.

Experience shows that a little fluid will be lost to the wall rock at and near the leading edge of the fracture. The loss of even a little fluid from a waste-cement slurry will materially increase its effective viscosity, and consequently, the tip of the fracture will, after a time, have difficulty in advancing. When this happens, a new fracture will form back near the injection well and move out along or near to the earlier fracture. In this way four or five grout-filled fractures have been formed by a single injection, and a built-in mechanism exists which will limit the extent of any single fracture.

When as much waste-cement slurry as seems desirable has been injected into a single slot in the casing, the bottom of the well is plugged with cement to a point a little above the slot, and a new slot cut at a new level a few feet higher up. The injections are then continued, forming a new system of fractures. This spacing of the fracture system is intended to prevent the building up of too much strain locally in the rock.

To make this concept work in practice, several problems must be solved. First, there must be assurance that all the fractures will be essentially horizontal. Second, a surface plant must be designed and constructed that will mix and inject the slurries. Third, a suitable waste-cement mix must be formulated. Lastly, practical measures must be devised for monitoring the operation and for determining the distribution and orientation of the fractures.

Figure 5 shows the four formations available at Oak Ridge for possible use for waste disposal by hydraulic fracturing. At the sites chosen for the field tests, and later for the actual use of the method, the land surface is underlain by 700 feet of gray calcareous shale of the Conasauga formation. This shale contains some thin beds of limestone the deepest of which, at the sites in question, is at 700 feet, where it marks a transition from the gray shale to the underlying red argillaceous shale. The red shale, 300 feet thick, is somewhat better bedded than the gray.

Below the Conasauga shale is the Rome sandstone, thick bedded, hard, brittle, and apparently unsuited to disposal by hydraulic fracturing. Below the Rome is the Chickamauga limestone which contains, as shown in the figure, two calcareous shale members probably suitable for disposal by hydraulic fracturing in that their well-developed bedding would encourage the formation of bedding plane or horizontal fractures. Below the Chickamauga is the Knox dolomite which, like the Rome, is composed of thick-bedded, hard, brittle rock in which the formation of vertical fractures would be all too likely.

(Figure 6) The four formations in the Oak Ridge area are contained within a series of large overthrust fault sheets which apparently moved to the northwest from the Appalachian Mountains at the time these mountains were uplifted. The fault sheets lie one on top of one another, like shingles. For this reason, all of the formations are exposed at the surface in long parallel strips, and by moving across the strike at right angles to these strips, it is possible to find a point where any formation may be found at any desired depth below the surface. Largely because 1000 feet is the greatest depth at which it is convenient to work, all our injections, except the first, have been made into the red argillaceous shale of the Conasauga formation at locations where this shale is between 700 and 1000 feet below the surface. This depth has also been sufficient to provide adequate containment for our actual disposal operations. Isolation of the red shale from overlying formations and surface water is shown by the sodium chloride present in the red shale, the presence in this shale of small quantities of gas under low pressure, and by the geothermal gradient.

The development of a sucessful method of waste disposal by hydraulic fracturing required the solution of four problems, the first of which was to determine the orientation of the fractures produced in the Conasauga shale at depths of 1000 feet at Oak Ridge.

Figure 7 shows the general arrangement of one of the field experiments which answered this question. The injection well was installed and slotted as described above. The pumping unit received water from the storage tank, and dry cement powder from the transit-mix truck. The cement slurry was pumped down the well under sufficient pressure to fracture the shale. At the wellhead, a small high-pressure matering pump added a radioactive tracer solution to the slurry so that the location of the slurry-filled fractures underground could be located by gamma-ray logging in test wells drilled subsequent to the injections. The test wells were cored, and some samples of the hardened grout recovered. The gamma-ray logging indicated clearly the depth of any grout sheet intersected by the test drilling.

In the so-called "second fracturing experiment" two injections were made, one at a depth of about 950 feet, a little above the Rome sandstone, and the second at a depth of a little over 700 feet, a little below the three beds which mark the contact between the gray calcareous shale and the red shale.

Figure 8 shows the lower grout sheet, as seen in plan. It is roughly an ellipse, about three times as long as it is wide, and as may be seen from the contour lines which show elevation in relation to sea level, the grout sheet slopes up to the north from the injection well. The edges of the sheet are probably more irregular than shown but a great many more test holes would be required to outline the sheets in any detail.

Figure 9 shows, in plan, the upper of the two grout-filled fractures formed during the second fracturing experiment. The fracture, in this case, moved out to the north and east, and although there is nothing in the plan to suggest it, the cores strongly suggest that there are several fractures, all lying in much the same nearly horizontal plane, but overlapping only in part. One fracture moved north, another northeast, and still another to the east.

Figure 10 shows the two grout-filled fractures in section, in this case a section parallel to the strike of the enclosing rocks. The lower sheet is nearly parallel to the contact between the shale and the underlying sandstone. The upper sheet is nearly parallel to the overlying limestone beds which mark the contact between the red shale and the gray. The fractures may, therefore, be said to be conformable; they conform to the structure of the shale.

Figure 11 shows the same two grout sheets, but in this case in a section parallel to the dip of the enclosing beds. Again it is clear that the fractures are conformable and have been guided by the bedding. Such fractures may loosely be called "horizontal" even though they and the enclosing beds have a dip of about 20 degrees; at least if the term horizontal is used in contrast to vertical, for vertical, or cross-cutting fractures will lead up steeply towards the surface.

These experiments, and others like them, have shown that fractures in the red shale member of the Conasauga at Oak Ridge are guided by the bedding and in this respect at least are suitable for waste disposal operations by hydraulic fracturing.

Having answered, at least provisionally the first question, that the fractures are essentially horizontal, the second question concerns the design of a surface plant capable of mixing the waste and the dry cement powder and pumping them underground.

Figure 12 is a diagrammatic representation of the plant. Waste is pumped to waste storage tanks adjacent to the plant through a pipe line. The tanks hold some 90,000 gallons, about all that can be disposed of in 1 day. The liquid waste is picked up from the tanks by the primary waste pumps which deliver it to the jet mixer at a pressure of about 100 psi. The solids, an already blended mixture of Portland cement, fly ash and clay, are fed through a hopper into the top of the jet of liquid where they are entrained through a short length of pipe into a small surge tank. There is sufficient turbulance in the jet and in the pipe to mix thoroughly the solids and the liquid, although it is not certain that there is enough shear to completely disseminate the solids in the liquid, for some of the solids may be left as small aggregates.

From the surge tank the waste slurry is picked up by the high pressure pump and forced down the well.

Probably the most difficult operation in the plant is control over the proportioning of liquids and solids. Two systems are used, but neither is entirely satisfactory. The first system employs a densometer, an instrument designed to control the proportioning of cement to water in the cementing of oil-well casing. A small pump forces some of the slurry in the surge tank through a loop of tubing in the densometer proper, where the weight of the loop is measured by the pressure in an air jet which is just able to support the loop in a horizontal position. Readings of the pressure in the air jet are converted to pounds per gallon of the slurry. Laboratory work will already have determined the weight, in pounds per gallon, of a properly proportioned slurry. Although the densometer works well in controlling the proportioning of cement to water, it is somewhat less satisfactory with the waste slurried. The waste is a sufficiently concentrated solution to have a density greater than water, and the proportion of solids added, about six pounds to the gallon, is not enough to make much change in the weight of the mixture. The densometer, in other words, is working on a relatively insensitive indication of the proportioning of the mix.

The second method of determining the proportion of solids to liquid in the slurry is to measure the rate of flow of both solids and liquid. Measuring the rate of flow of the liquid is easy; measuring the rate of flow of the solids is a little more difficult. An inverted cone is placed under the flow of solids as they fall into the top of the jet mixer, and the force exerted on the cone is measured. This mass flow meter is calibrated in pounds per minute, and, in conjunction with an indication of gallons per minute of flow of the liquid waste, makes possible in theory an accurate control of the proportioning. Unfortunately, the mass flow mater is neither as sensitive nor as accurate as could be wished.

The jet mixer itself is set to mix a little more solids than are desired with the liquid waste. However, there is a bypass around the jet mixer through which liquid waste may be fed directly into the surge tank. By controlling the rate of flow through this bypass, the proportion of solids to liquid in the slurry may be reduced to the desired ratio.

The third problem is the formulation of a cement-clay mix that will have the desired properties. The solids which are added to the liquid waste perform two related functions. First, the cement on setting converts the liquid slurry into a solid and so robs it of its mobility. Second, the solids in the slurry, and the new solids that form as the cement sets, must hold tightly to the radioactive materials in the waste. Also, the solids must not settle in the liquid before it has set of there will be a liquid phase left over that will not harden.

Attapulgite clay is added, in addition to the cement, to thicken the liquid and keep the solids in suspension. In this, the degree of mixing is important, for if the clay is not thoroughly dispersed there will be some phase separation. In addition to the attapulgite some grundite clay, a variety of illite, is also added, as the members of the illite family of clays have the ability to strongly adsorb cesium, and ^{137}Cs is the predominant radioactive nuclide in the waste.

Portland cement in setting sets free some calcium hydroxide which is later slowly leached out of the concrete if it is exposed to the weather. Because strontium is so similar chemically to calcium, some strontium hydroxide will also form, although most of the strontium will be incorporated into the new crystals of calcium aluminum silicate, which give the set cement its strength. When a highly siliceous material like fly-ash, the fine ash that is removed from the smoke in the staks of coal-burning power plants, is added to cement and the two then mixed with water, the fly-ash reacts with the calcium hydroxide as it is set free and the fly-ash sets up hard also. For this reason the Portland cement used in making the waste slurries is "diluted" with an equal weight of fly-ash, which not only reduces the cost of the mix, but helps to bind up the strontium hydroxide, for it also reacts with the fly-ash and, with the calcium hydroxide, forms a pozzolanic cement.

The fourth general problem to be solved, if disposal by hydraulic fracturing was to become practical, was to find methods of monitoring the operation, and more particularly methods to locate the grout sheets underground and determine their orientation without the expense of drilling test wells from the surface. The most important method, although admittedly somewhat indirect, is to note carefully the pressures required during an injection. Figure 13 shows a typical pressure pattern observed during an injection. About 40 minutes before the actual injection began the well was "broken down" with a few hundred gallons of water; the pressure required was about 3700 psi, which fell rapidly at first and then more slowly after pumping had stopped. When the waste injection began, the pressure required initially was about 3200 psi. During the first 20 minutes, the pressure fell to about 2500 psi and then continued to fall more slowly until it reached 2200 psi after some 140 minutes. The pumping was stopped briefly about half way through the injection, and during this interval the pressure dropped about 200 psi. When pumping was resumed, a slightly greater pressure was required briefly. This pattern of injection pressures is very similar to those seen during all of our injections and is presumed typical of the pressure pattern when a horizontal fracture is being formed. In particular, the observed pressures are all well above the pressure due to the weight of the rock overlying the fracture, which at a depth of 850 feet would be 627 pounds as measured by a pressure gauge at the land surface attached to a water-filled pipe. It is generally agreed that if the fracturing pressure is greater than the weight of the overlying rock, the fracture may be either horizontal or vertical, but that if the fracturing pressure is less the fracture must be vertical. The relatively high pressures recorded are, therefore, not proof that the fractures are horizontal, but if vertical fractures were to form the pressure hystory would presumably be different and the overall pressures probably lower.

More direct evidence that the fracture is horizontal can be supplied by gamma-ray logging of monitoring wells drilled down through the disposal area and cased prior to the waste injections. Figure 14 shows one such well which has been intersected by three grout sheets. Logging will show three sharp peaks where these fractures intersect the monitoring well. By logging each of a network of such wells following each injection, it is possible to tell where that injection has gone by nothing the new peaks on the logs.

The waste injections into the horizontal fractures produce a widespread uplift at the surface; the space in the fracture which is occupied by the waste is provided by this surface uplift. A network of bench marks was constructed in the disposal area, with the more distant bench marks out beyond the area that will be affected by the surface uplift. Periodic releveling of these has shown a broad, gentle uplift of the area. This surface uplift would be much the same even if a vertical rather than a horizontal fracture should form so that measurements of surface uplift are hardly a method for determining fracture orientation. However, if as a result of the uplift a steeply dipping fault should form in the cover rock overlying the fractures, the resulting uneven surface uplift might well be detected by the leveling. The formation of vertical rather than horizontal fractures, and a failure of the impermeable cover rock which provides a seal overlying the injected sheets of waste, are the two most serious modes of failure against which we need to be on guard.

A second method of testing for possible failure of the rock cover is by use of the "rock cover test wells," one of which is shown in Figure 14. These wells are first drilled about 6 inches in diameter to a depth of about 550 feet, and a 4-inch casing cemented in to this depth. Then a hundred feet of 3-inch open hole is drilled below the bottom of the casing so that the total depth of the finished well is about 650 feet. An attempt is then made to pump water down the well at a surface pressure of 75 psi. These wells at first take water at this pressure at a rate of one or two gallons an hour, but after a few hours they will take no more. By repeating this test periodically after every few waste injections, it is possible to determine if the rock cover adjacent to one of these test wells has become more permeable, as it would if incipient fractures were starting to develop. This method of monitoring the cover rock assumes that enough is known about the rock mechanics of the disposal operation so that the test wells can be located where cracks in the cover rock will first appear, and there is no assurance that this is yet possible.

Figure 15 is a somewhat diagrammatic representation of the geologic structure at the site of the shale fracturing waste-disposal plant and of the pattern formed by the several grout sheets. The seven observation wells and the injection well are arranged in a rough north-south cross section, although the distances between the wells have not been retained. The natural gamma-ray log of each well is shown, and by inspection of these it is possible to follow from well to well the location of the "three limestone beds" which mark the contact between the gray shale and the red shale in the Conasauga formation, and, with the help of certain information from the cores of these wells, the contact between the Conasauga and the Rome sandstone may be similarly followed. Other stratigraphic horizons within the

Conasauga may be similarly identified. The first point of note is that the geologic structure in the area so outlined is essentially horizontal. The total north-south distance represented by the section is about 250 feet; if the local dip were 20°, that is, equal to the general dip in this area, the structure would be some 90 feet higher at the north end. The levels where the various test injection, and the operational injections of real intermediate level waste (marked ILW), were made are indicated on the injection well, and straight lines indicate where these various injections were found in the test wells. The identification is not always certain. The grout samples found in the cores can be correlated with the several injections only on the basis of their general level of activity. Any new grout sheets located by gamma-rays logging in the cased observation wells after each injection can now be identified as resulting from that injection, but until recently the levels far exceeded those for which the instrument was designed, and the results were ambiguous. The pattern of the grout sheets, as indicated in Figure 15 is, however, substantially correct. In particular, several of the later injections intersected well N150 at points below several of the previous injections. The problem in part is due to a barrier between the injection well and well N100, which forced some of the injections up as much as 40 feet. Later injections broke through this barrier, which is probably a belt of closely folded shale, and so came through at a lower level. More importantly, however, the general pattern formed by the fractures is unmistakably horizontal, that is, conformable, and even where the grout sheets have been deflected from the horizontal, they apparently have returned to follow the bedding.

Figure 16 illustrates a second use which has been found for the so-called rock cover monitoring wells, or water-level observation wells as they are called in the figure. These wells are cased down to a depth of between 500 and 600 feet, below which about 100 feet of uncased hole is drilled. The wells are normally filled with water. During some of the earlier injections, a change in water level was noted; in some wells the water level came up and the wells overflowed; in others the water level fell slightly. The same wells acted differently during different injections. Later, a better appreciation of what as happening was obtained by capping the wells and equipping each with a pressure gauge.

When the injected grout sheet passes under one of the rock cover monitoring wells, the shale in the vicinity of the well is compressed; and a little water is squeezed into the open hole section of the well, raising the pressure. In areas adjacent to, but not underlain by, the grout sheet, the shale is uplifted by shearing forces transmitted from the area of direct uplift, and the shale is either not compressed or may even expand slightly.

These relations are illustrated in Figure 17. The grout sheet formed by injection ILW-2A apparently moved north from the injection well, passing under well N200E after about 40 minutes, when the pressure in this well started to come up. After about 270 minutes the pressure in this well started to fall; the inference is that a new fracture had formed back near the injection well leading out in some other direction, so that well N200E was no longer in the zone of compression. The pressure in well S200 at first remained constant, and then fell slightly, suggesting that the grout sheet did not move south. During other injections these relations were reversed, the pressure in well N200E falling slightly while there was a marked rise in the pressure in well S200. On such occasions the fracture probably moved out to the south. The rock cover monitoring wells, therefore, may be used to deduce the suburface distribution of the grout sheets.

SLIDE 18 ORNL Hydrofracturing Equipment (Photo 65016)

View of the ORNL hydrofracturing equipment showing solids feeders and shielded cell containing pumps and other equipment.

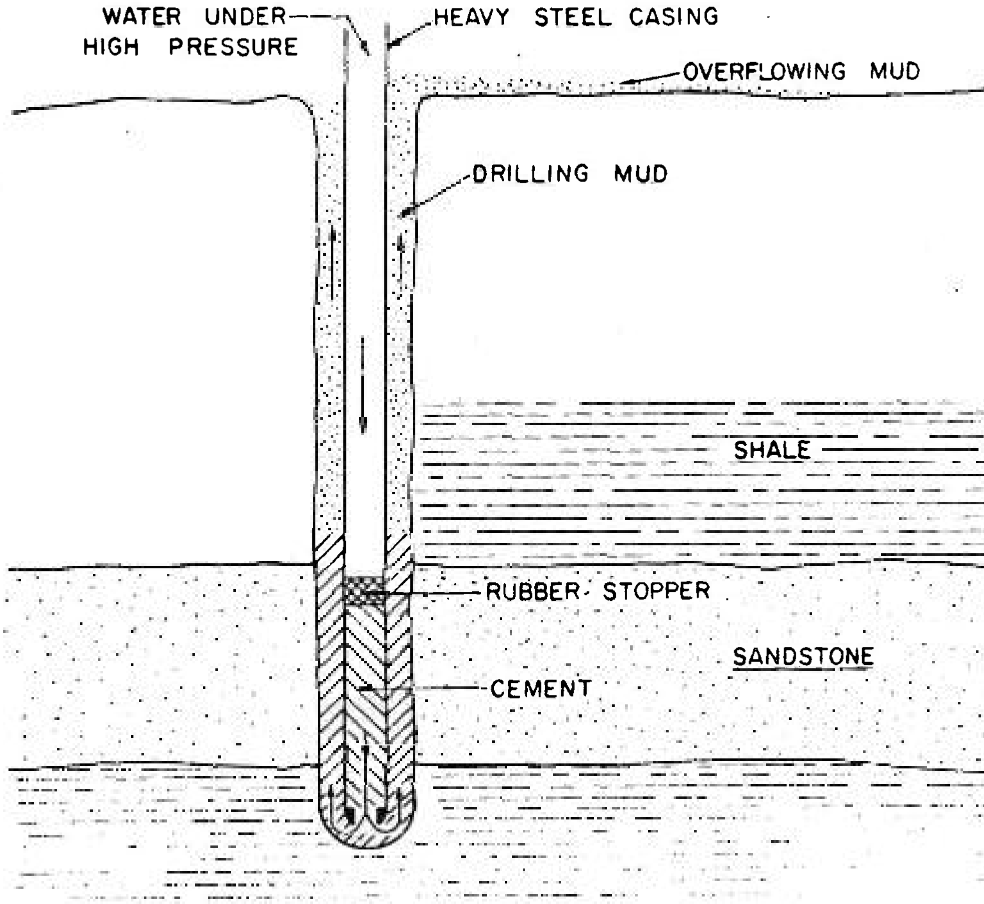
SLIDE 19 Summary of Cost Estimates for Disposal of ORNL Wastes by Thydraulic Fracturing (67-3871)

The total estimated cost of disposal by this method is based on its anticipated use for the disposal of ORNL waste evaporator residues; that is, injection of 80,000-gal batches at 4- to 6-month intervals with no interest charges for the capital investment and with the calculations carried out for both a 4 x 10^6 gal ultimate capacity and a more realistic 10^7 gal capacity. The total cost of $0.20 to $0.30/gal can be compared with an estimated $0.30 to $0.35/gal for permanent tank storage of ORNL intermediate-level wastes. It should be pointed out that tank storage does not solve the waste disposal problem, only postpones it. Some of the ORNL waste tanks had an estimated life of 20 years when constructed. They are now 22 years old. Hydraulic fracturing therefore appears to be not only slightly less expensive than tank storage, but it also has the added advantage of permanently removing the radioactive materials from the biological environment.

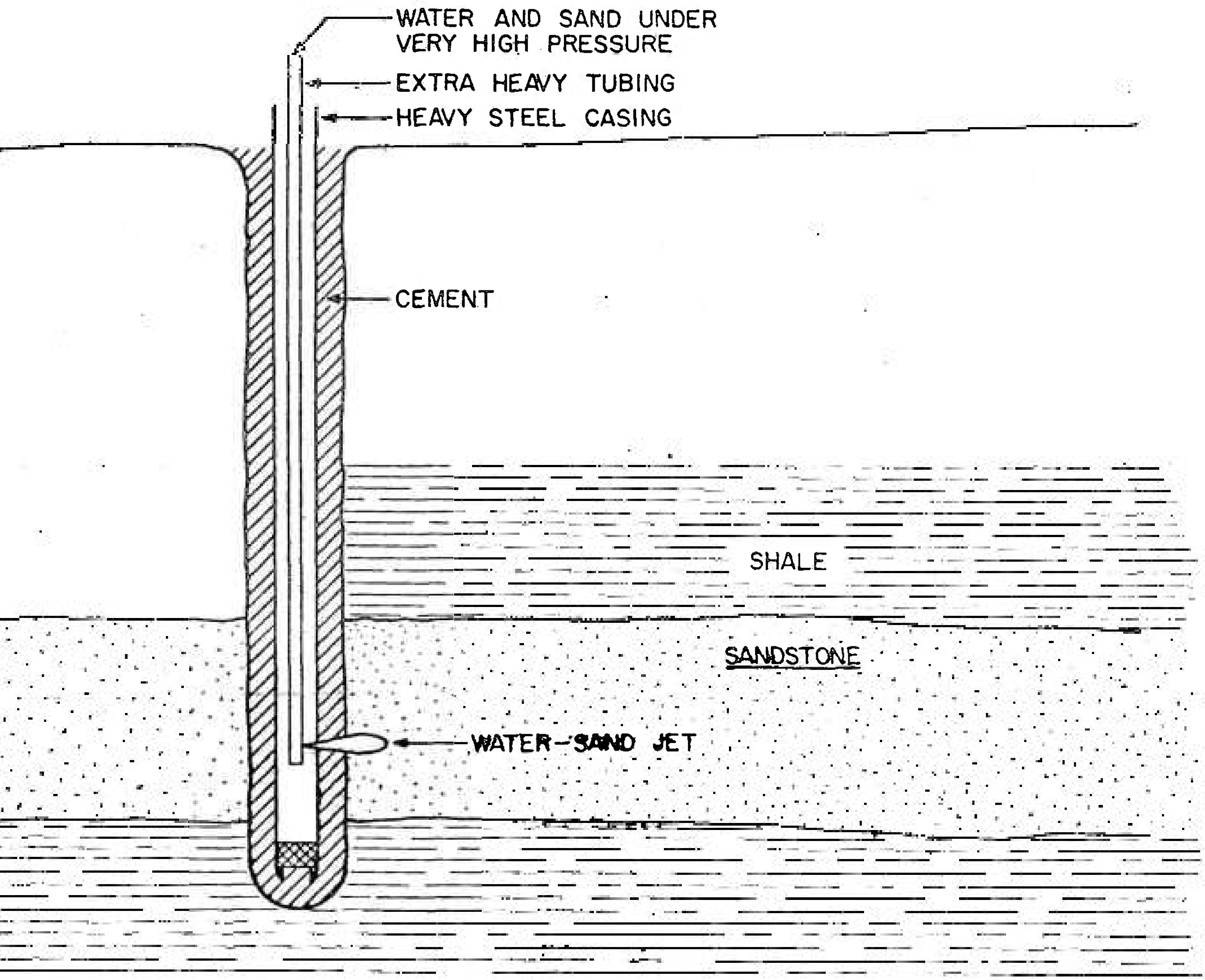
REFERENCES AND EXCERPTS FROM:

1. W. C. McClain, "Hydraulic Fracturing as a Waste Disposal Method," *Disposal of Radioactive Wastes into the Ground,* Proceedings of a Symposium, Vienna, May 29 – June 2, 1967, jointly organized by the IAEA and ENEA, SM-93/10, pp. 135-145.

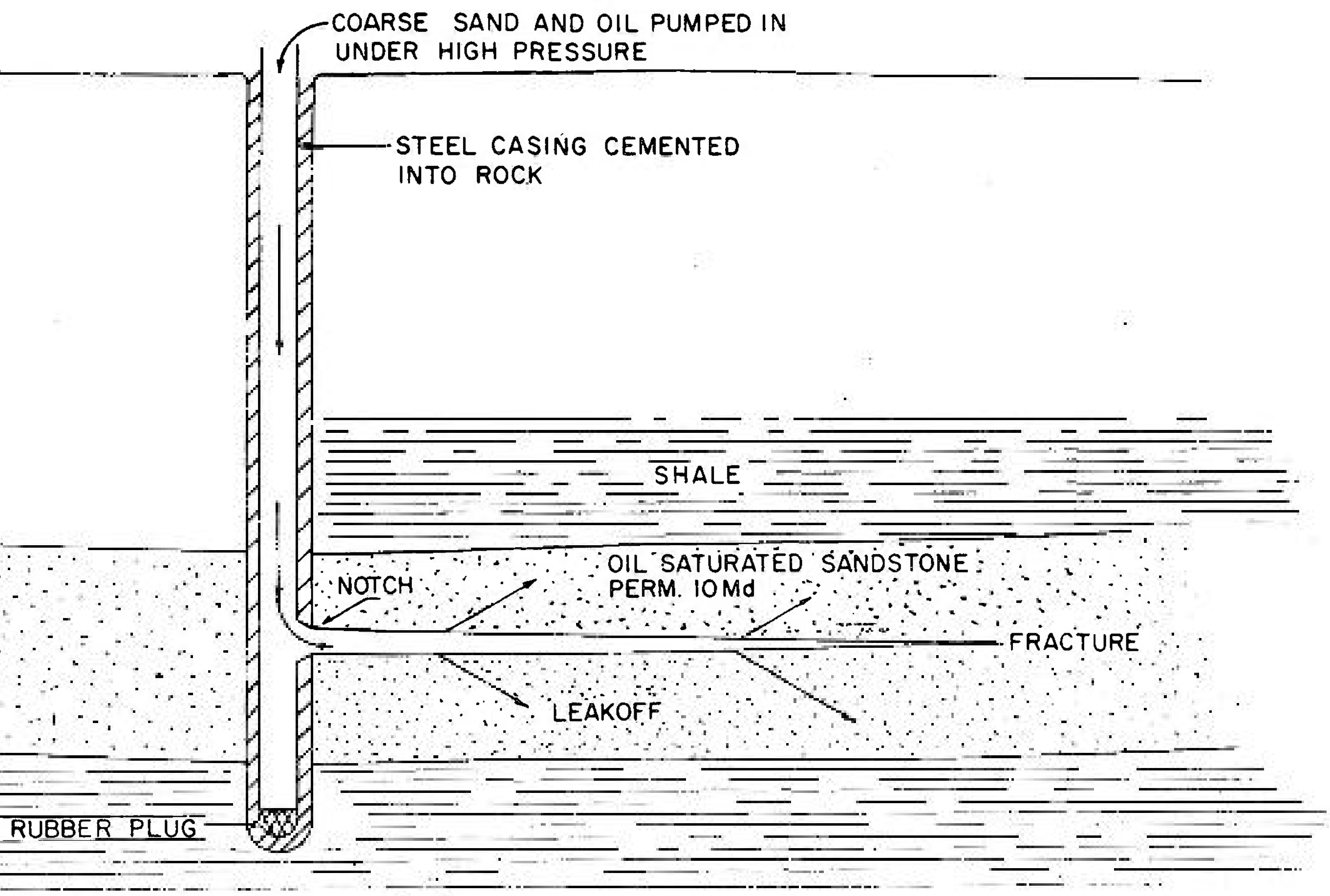
2. W. de Laguna *et al., Engineering Development of Hydraulic Fracturing as a Method for Permanent Disposal of Radioactive Wastes,* ORNL-4259.



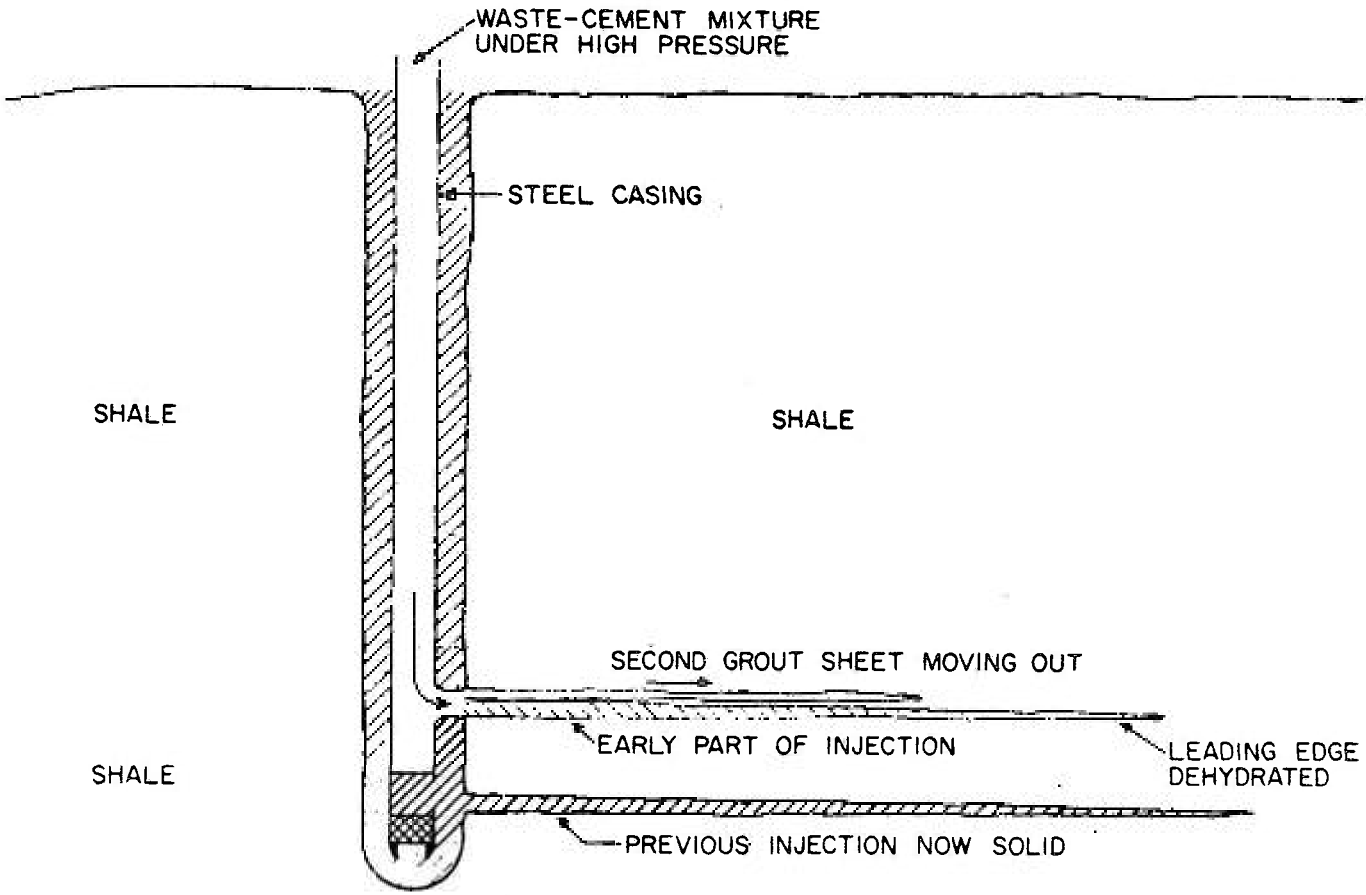
CEMENTING IN CASING



CUTTING SLOT

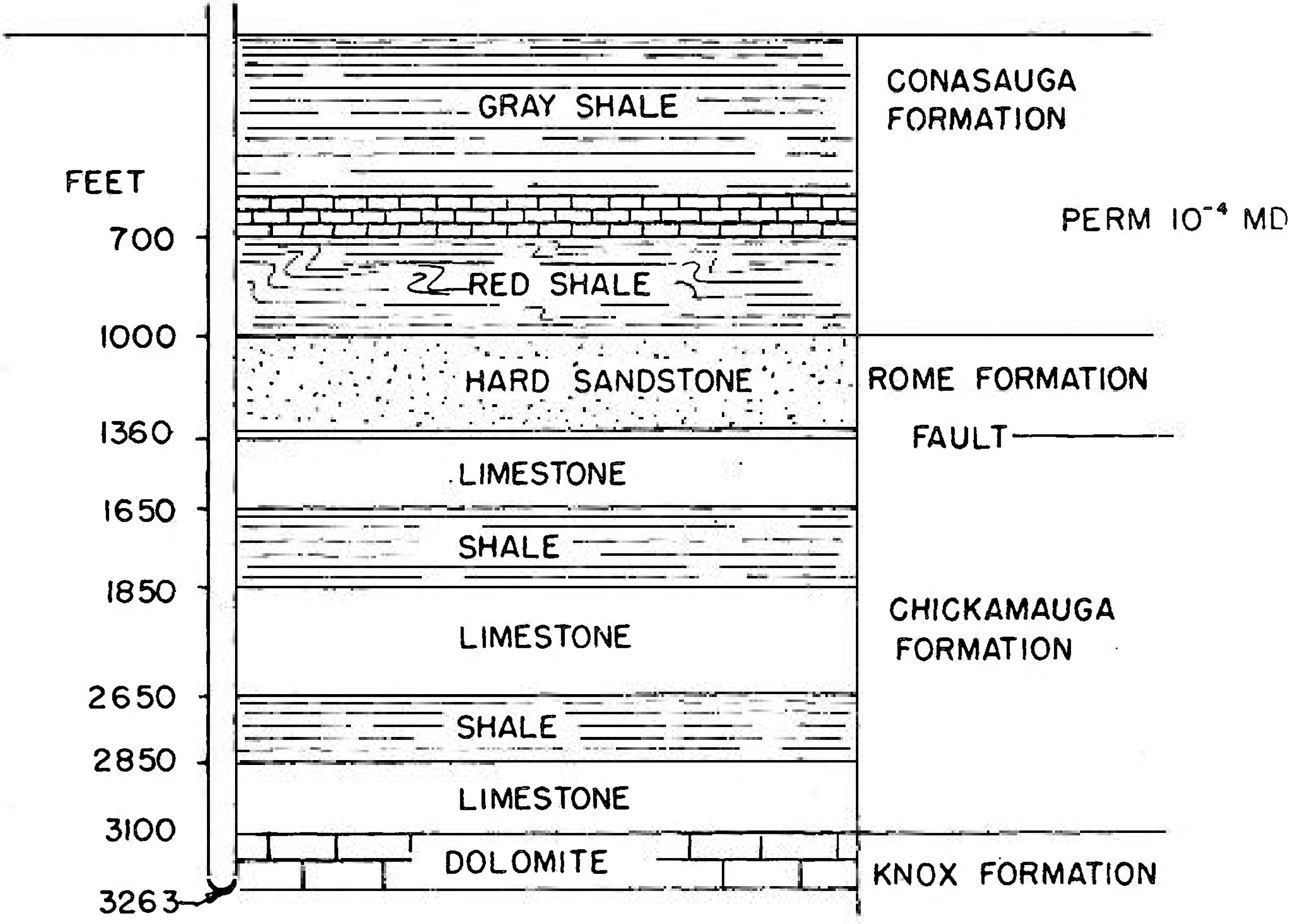


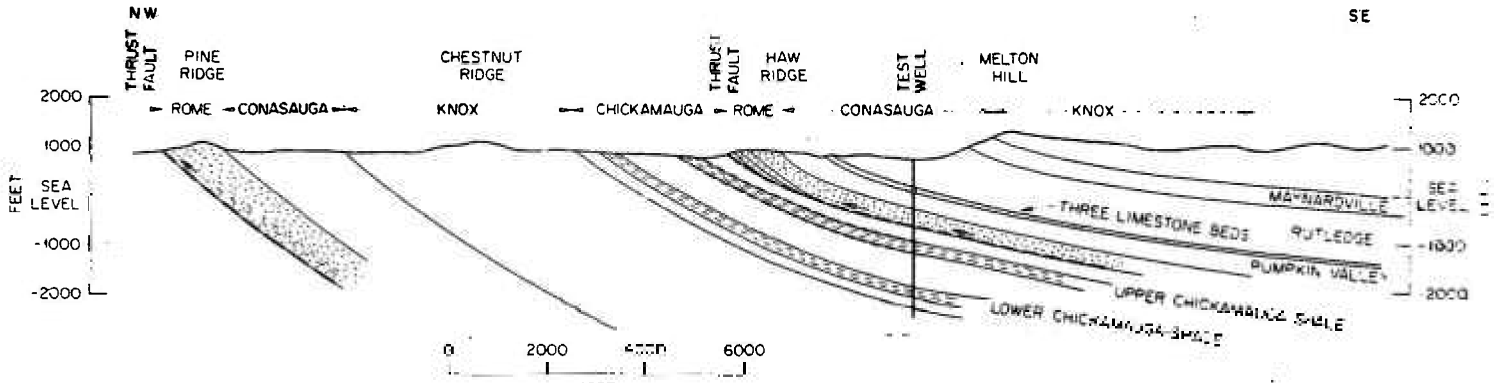
FRACTURING FOR OIL PRODUCTION



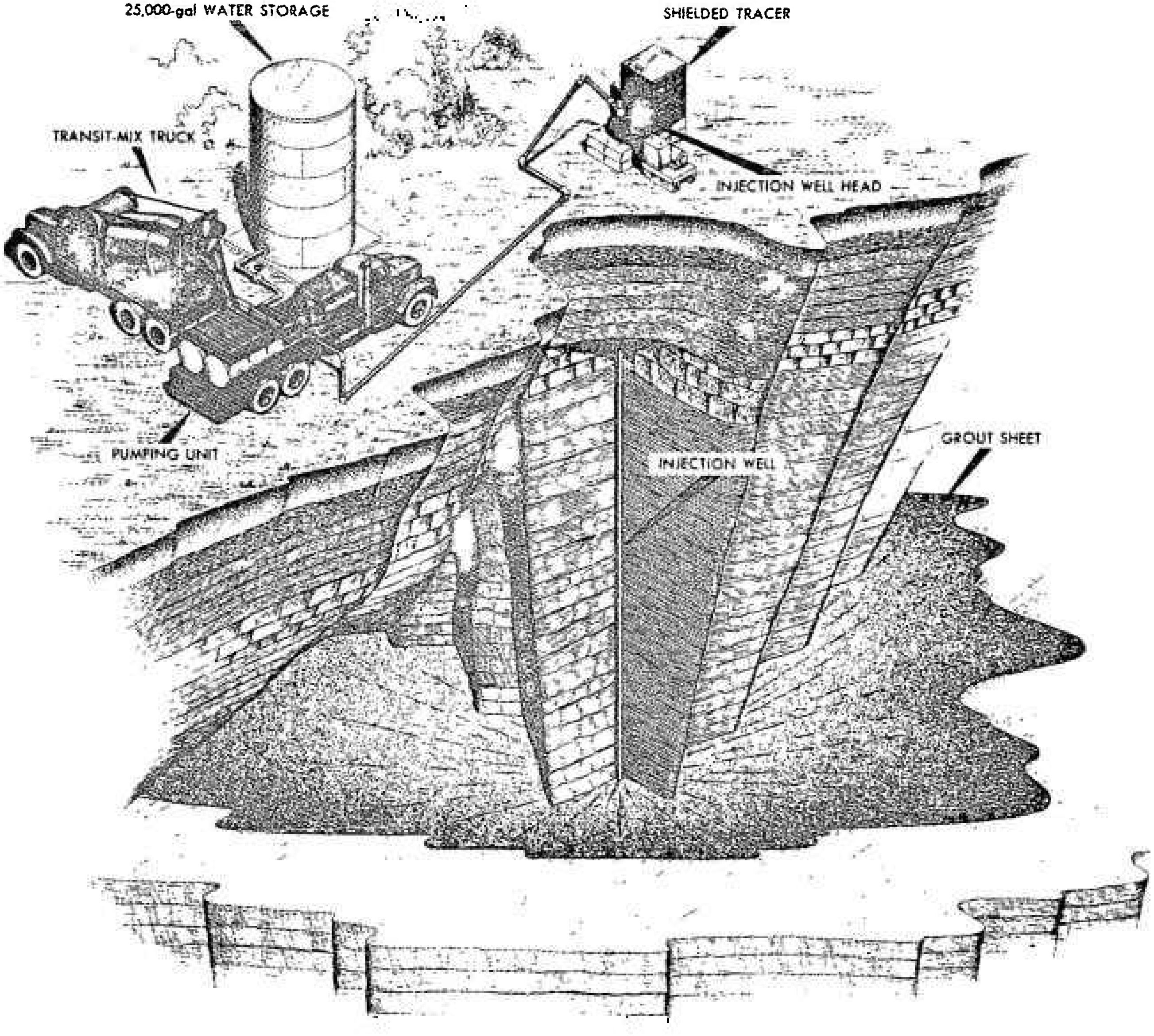
WASTE-CEMENT INJECTION

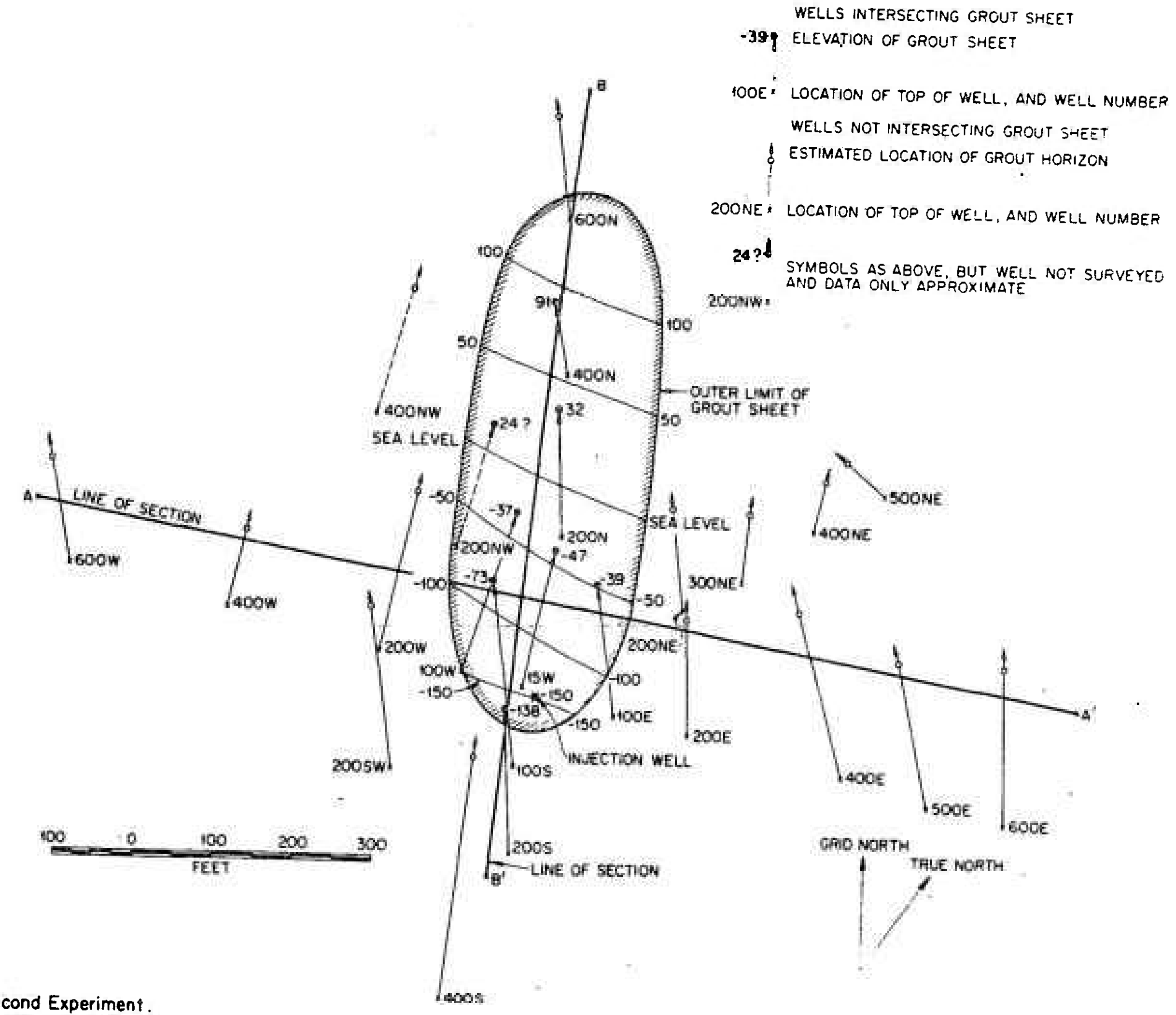
SUBSURFACE GEOLOGY ORNL
FRACTURING PLANT SITE



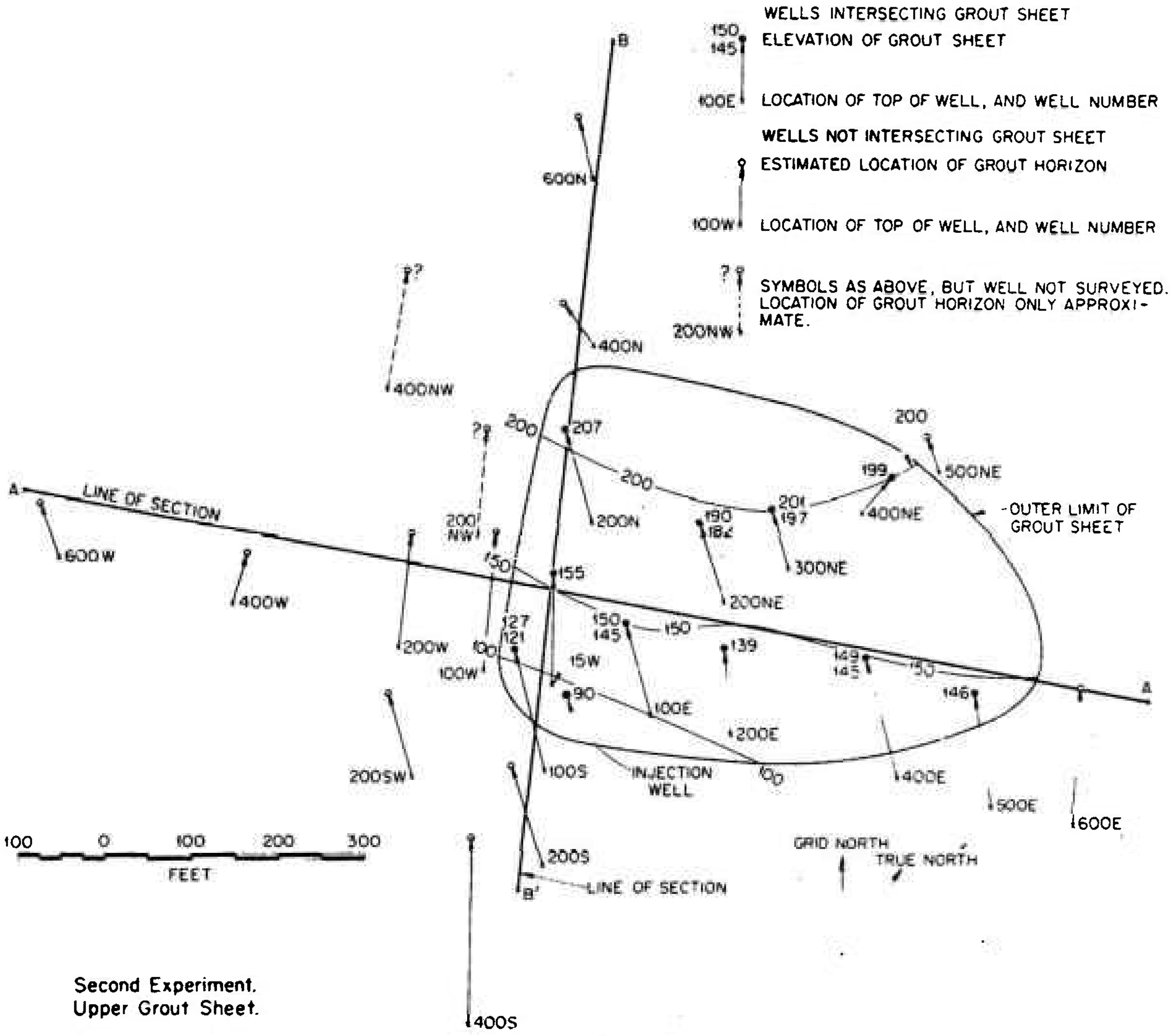


Geologic Section Through Test Well at Fracturing Plant Site.

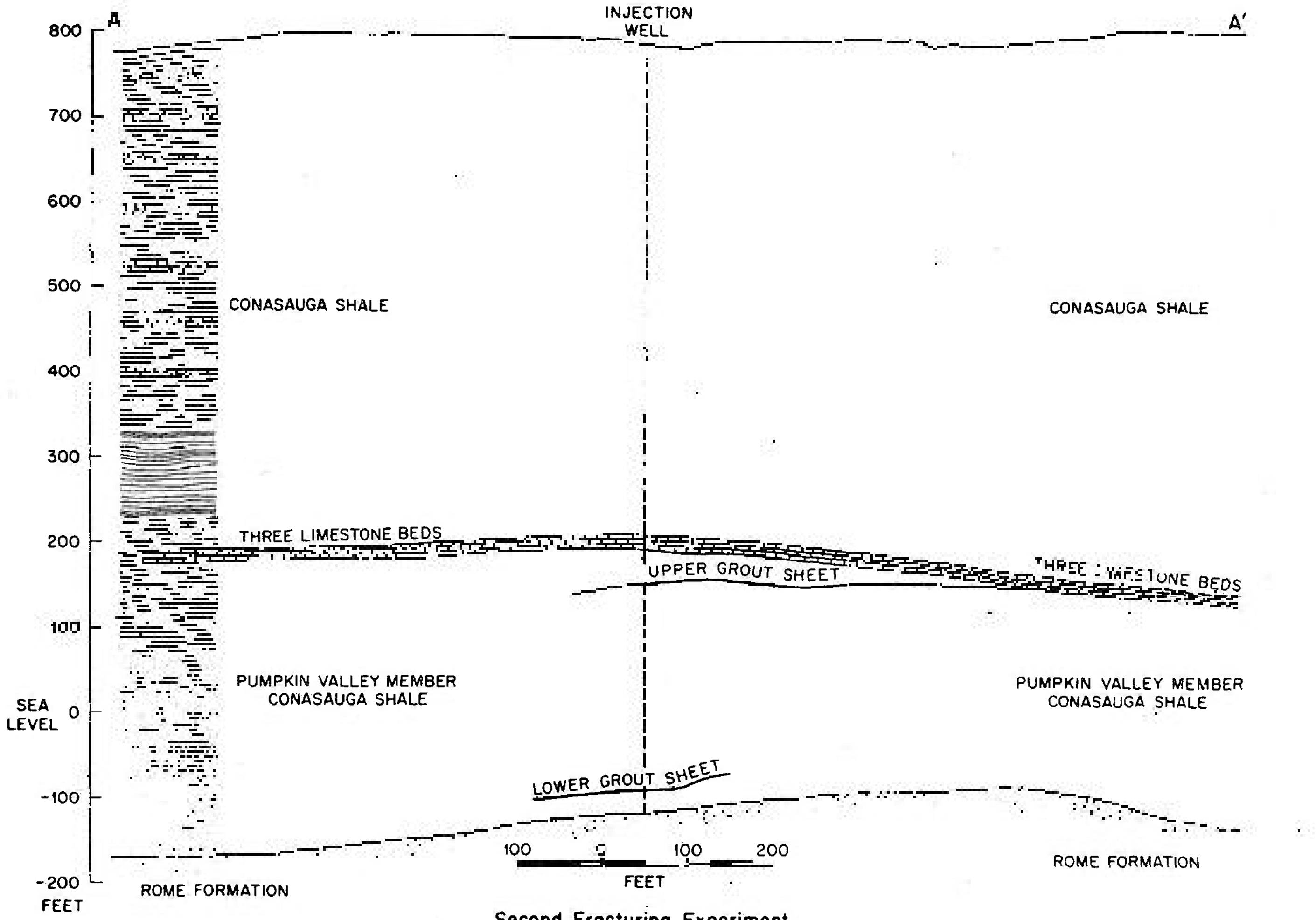

25,000-gal WATER STORAGE
SHIELDED TRACER
TRANSIT-MIX TRUCK
INJECTION WELL HEAD
PUMPING UNIT
INJECTION WELL
GROUT SHEET



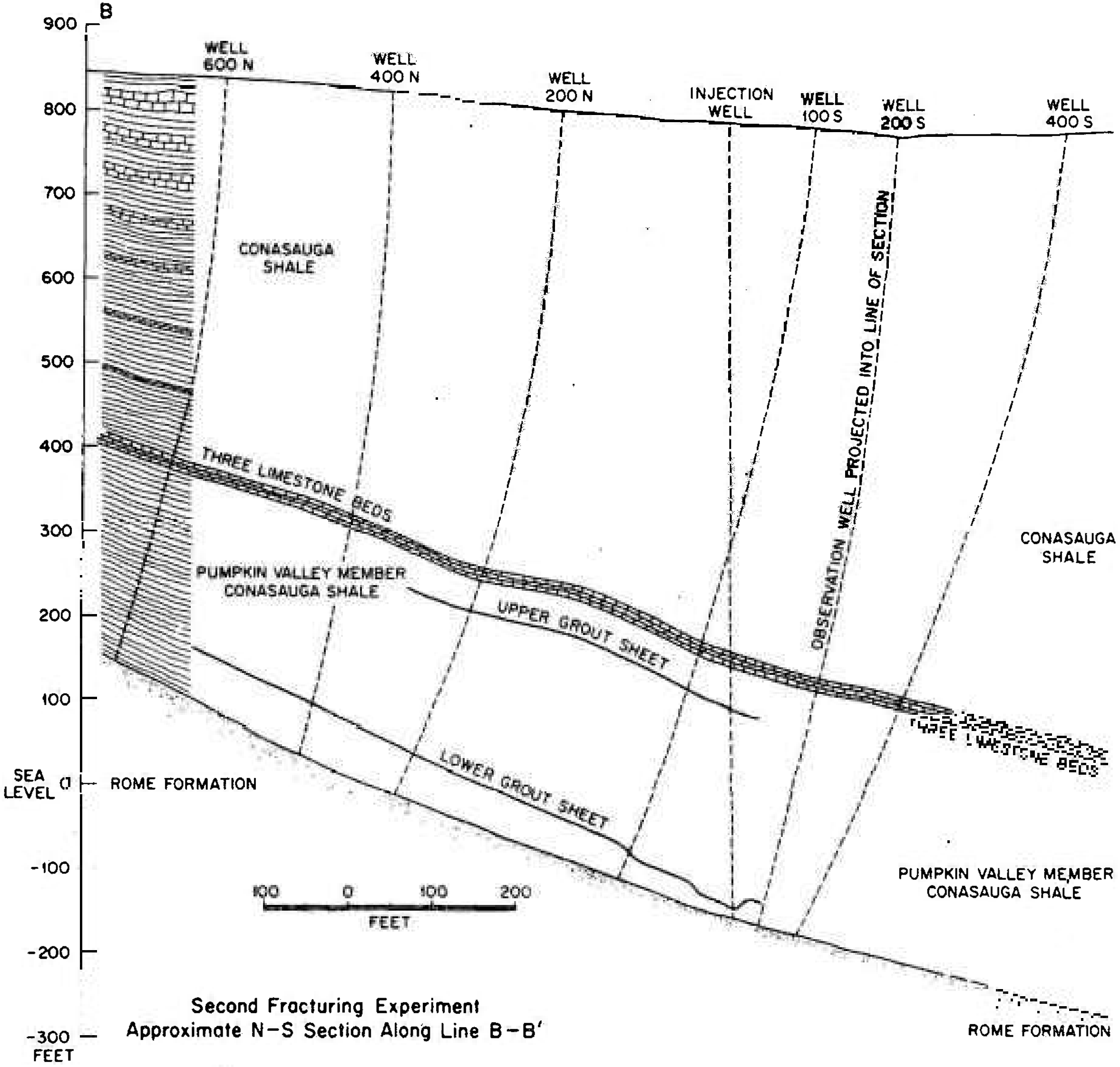
Second Experiment.
Lower Grout Sheet



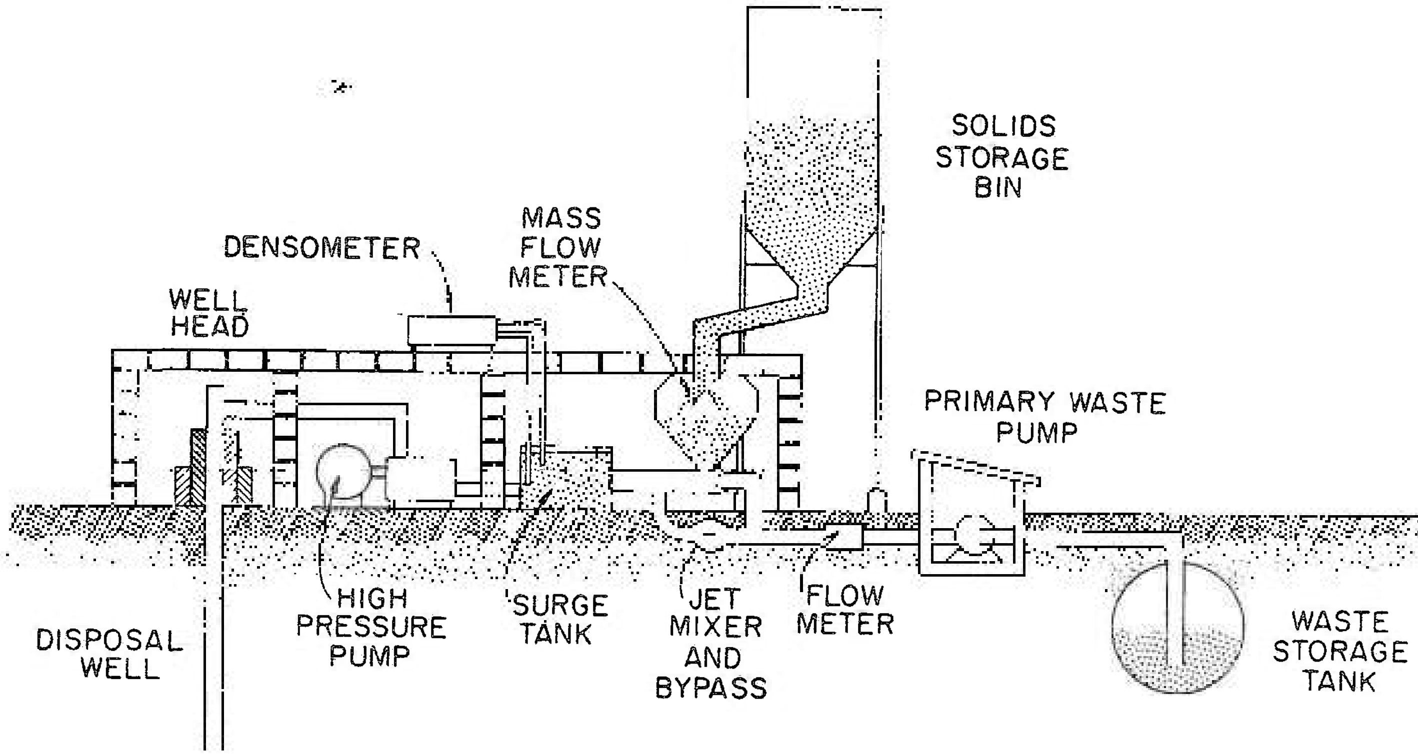
Second Experiment.
Upper Grout Sheet.



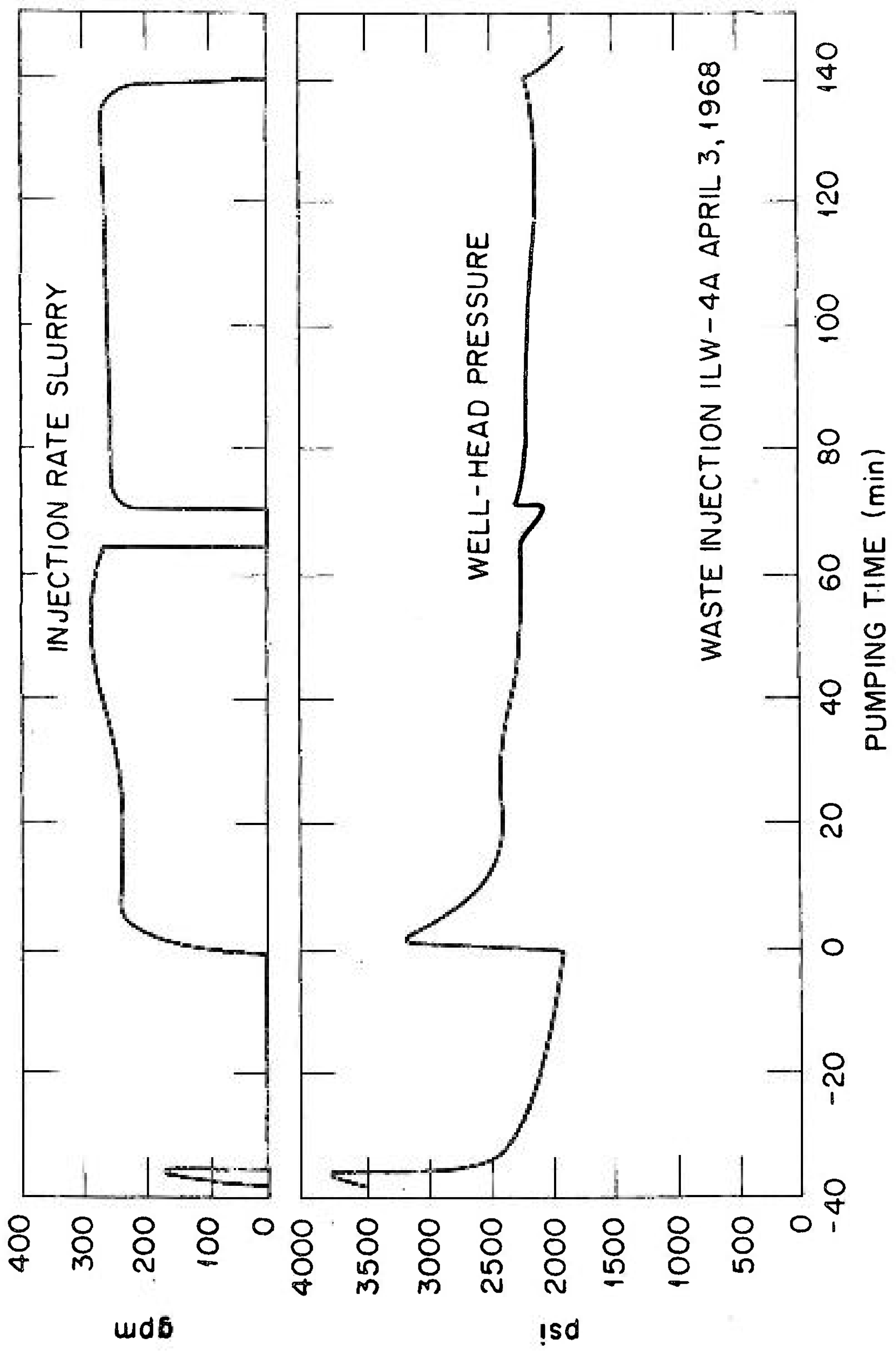
Second Fracturing Experiment
Approximate E-W Section Along Line A-A′

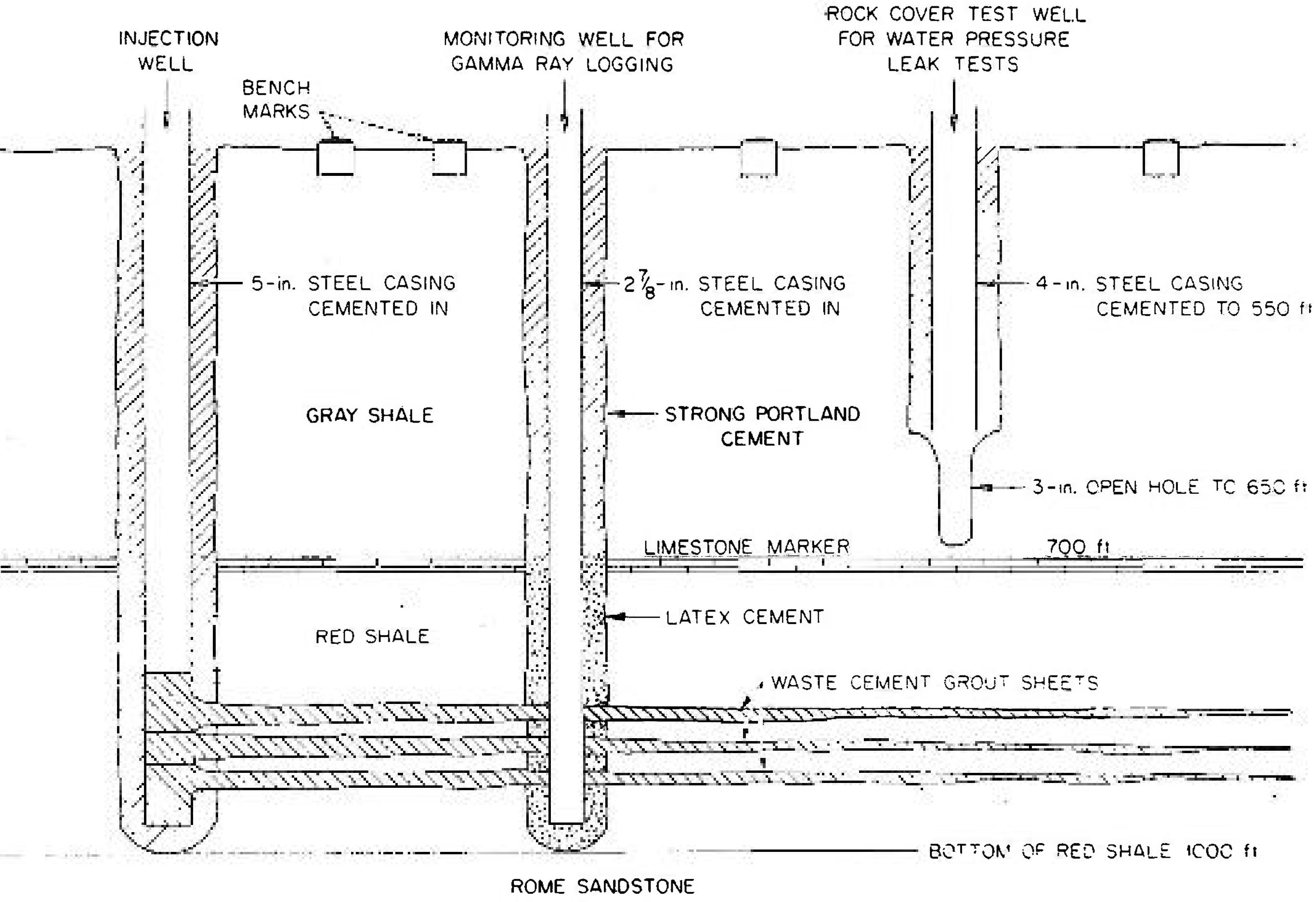


Second Fracturing Experiment
Approximate N–S Section Along Line B–B′

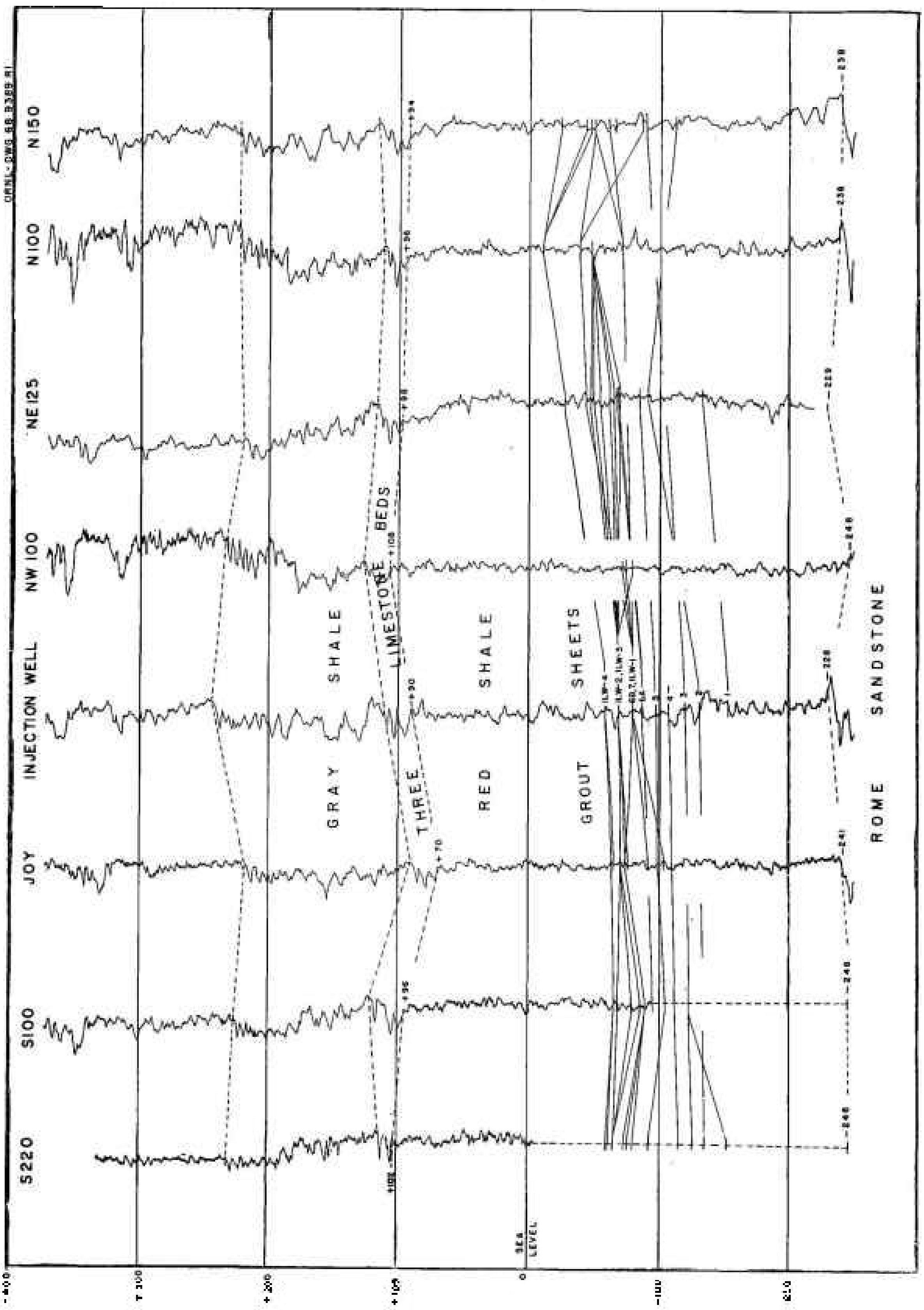


Plant for Waste Disposal by Hydraulic Fracturing.


INJECTION RATE SLURRY
WELL-HEAD PRESSURE
WASTE INJECTION ILW-4A APRIL 3, 1968
gpm
400
300
200
100
0
psi
4000
3500
3000
2500
2000
1500
1000
500
0
-40
-20
0
20
40
60
80
100
120
140
PUMPING TIME (min)



. Plant Layout.


ORNL-DWG 68-3389 R1
S220
S100
JOY
INJECTION WELL
NW 100
NE125
N100
N150
GRAY SHALE
LIMESTONE BEDS
THREE
RED SHALE
GROUT SHEETS
ROME SANDSTONE
+400
+300
+200
+100
0
SEA LEVEL
-100
-200
+94
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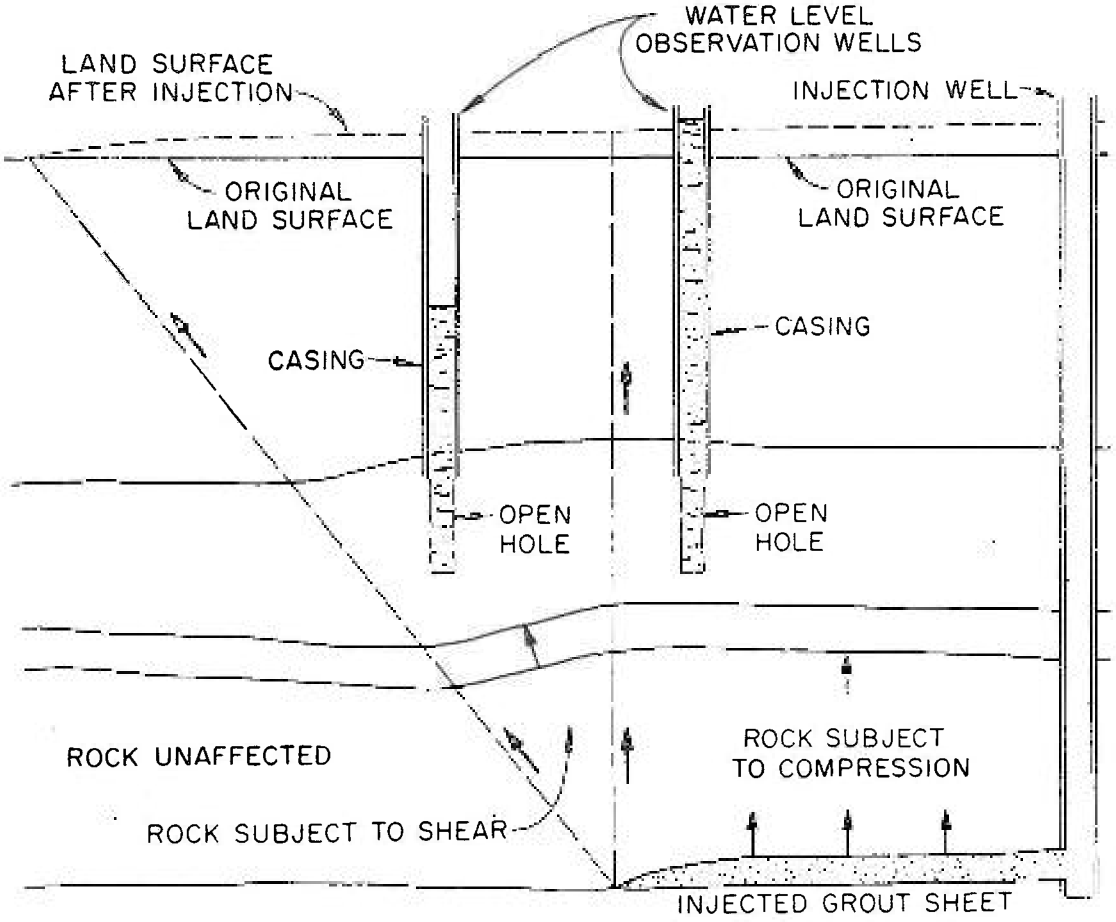
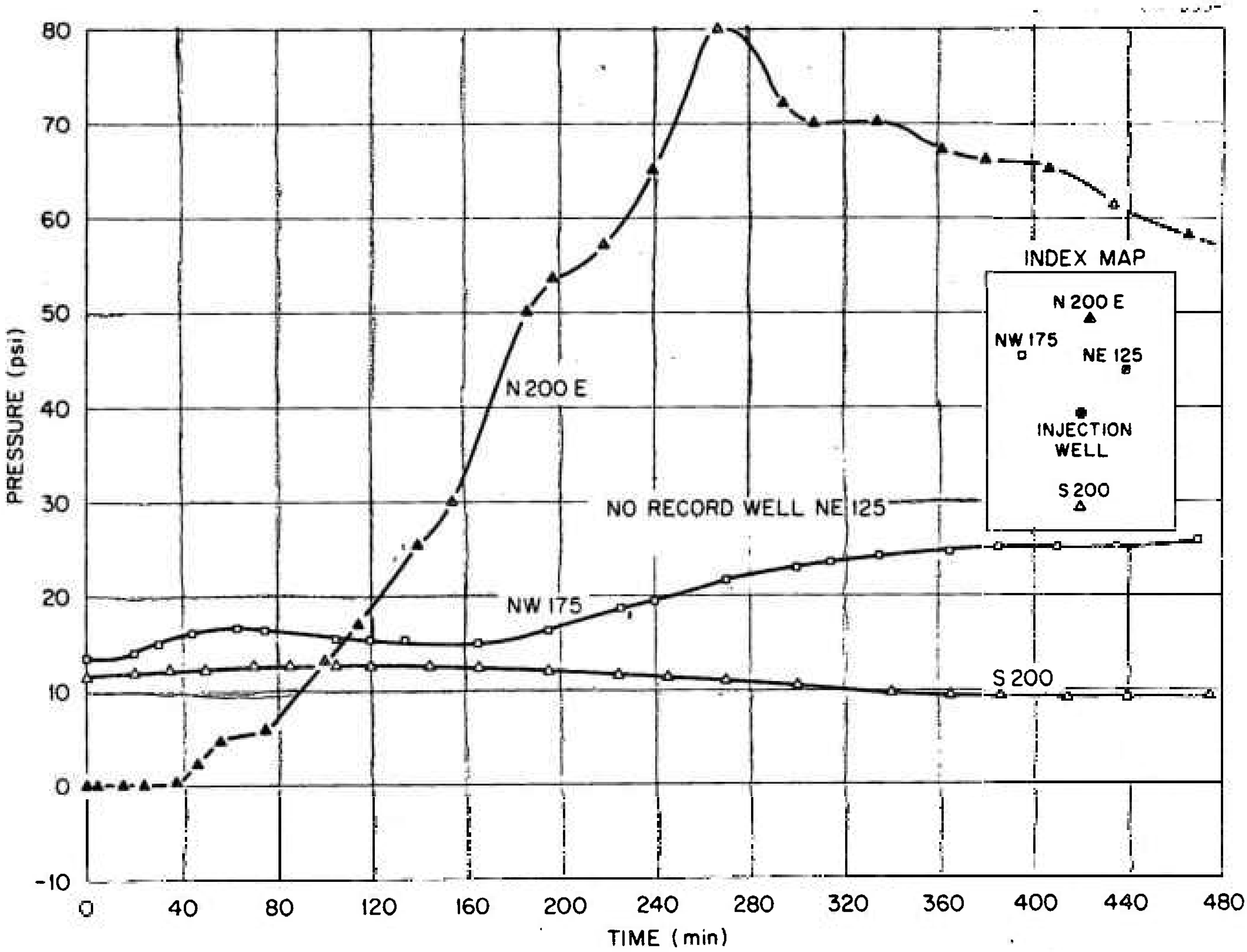
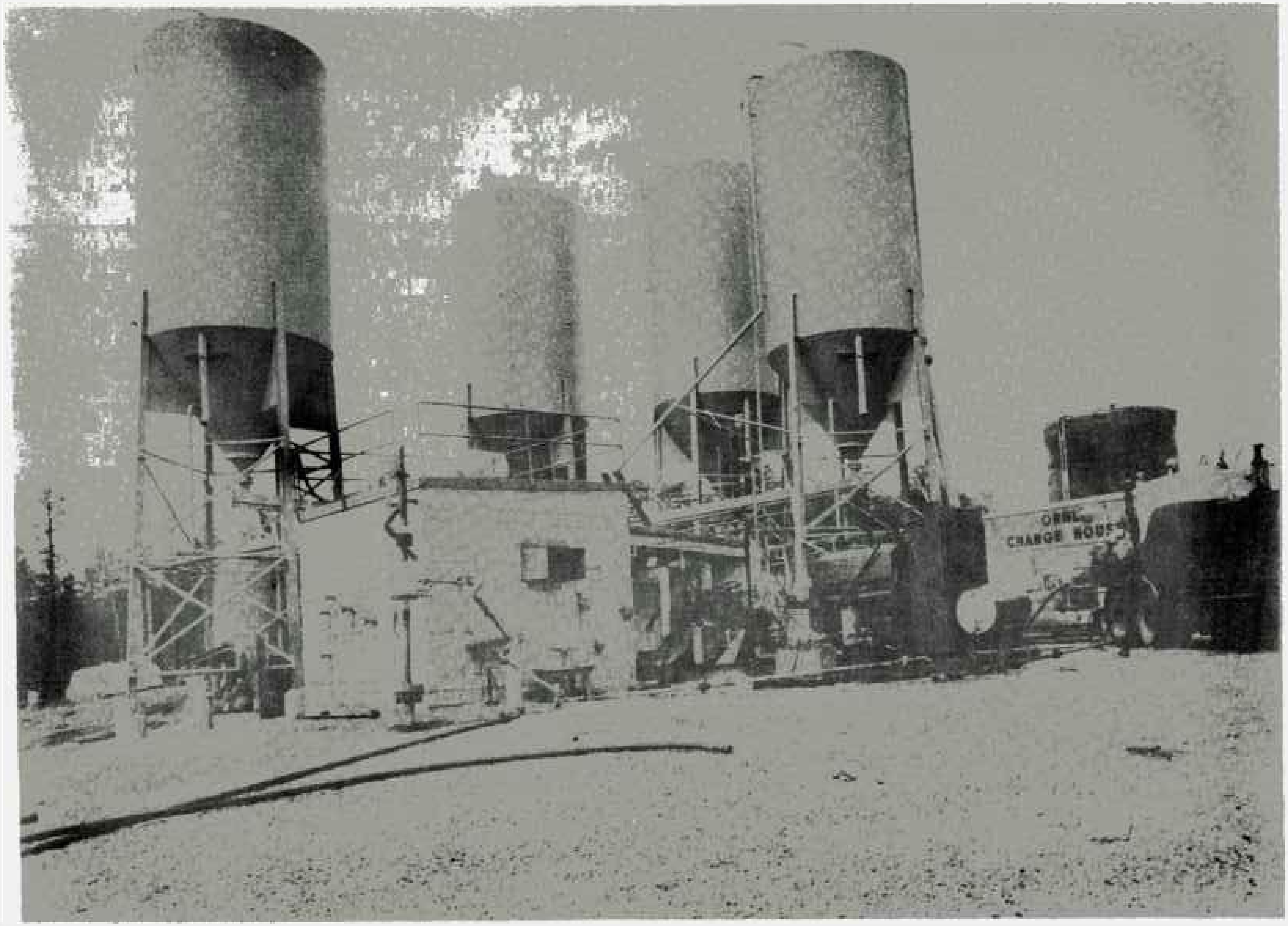


Stresses in Rock Due to Injection of Grout



Injection ILW-2A, April 20, 1967; Pressure Changes in Rock Cover Monitoring Wells.


ORNL
CHANGE HOUSE

SUMMARY OF COST ESTIMATES FOR DISPOSAL OF ORNL WASTES BY THYDRAUTIC FRACTURING.

	Cost per 80,000 gallon injection ($)	Unit Costs $/ gal of waste injected	
		4 x 10^6 gal. total capacity	10^7 gal. total capacity
Capital Investiment Amortization ($500,000)		0.125	0.050
Dry solids	4800	0.060	0.060
Halliburton Contract	4000	0.050	0.050
ORNL Direct expense	4000	0.050	0.050
Total	12,800	0.285	0.210
	(operating only costs = $0.16/gal.)		