

CHELATED IRON CHEMISTRY FOR
H₂S OXIDATION COMES OF AGE

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Introduction

H₂S is a toxic and odorous gas that can seldom be tolerated in the feed gases to industrial processes or in the waste gases discharged from them. There are only two effective ways to get rid of H₂S - burn it to SO₂ or oxidize it to sulfur.

In the past, much of the unwanted H₂S was incinerated or flared. The SO₂ produced is a contributor to acid rain problems and many industries are coming under stringent emission regulations. This has led to an upsurge in interest in processes which can remove H₂S and convert it to sulfur. The chelated iron scrubbing approach, represented by the LO-CAT(R) Hydrogen Sulfide Oxidation Process, is the fastest growing of these processes.

Aqueous solutions of chelated iron have been known to catalyze the reaction between O₂ and H₂S to form elemental sulfur for over 25 years. Broad application has only occurred during the past five years during which time the LO-CAT process has gained acceptance in a variety of services.

This paper will describe enough of the chemistry to understand how the process works and what the main problems have been, and what it takes to make a process which runs well, has very good efficiency and has a degree of forgiveness for operators.

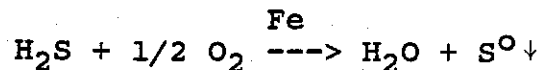
Process Chemistry^{1,2,3}

There are two ways a chelated iron scrubbing system can work; the iron can simply be a catalyst for the H₂S-oxygen reaction, or it can perform as a catalytic reagent and actually take part as a reagent in different parts of the process.

In the first case, the H₂S and oxygen are both in the same gas stream. Usually this is an air stream used to ventilate a process. Examples of such aerobic processes are:

- Cellophane manufacture
- Rayon plants
- Sewage plant
 - Dissolved air floatation units
 - Lift pump enclosures
 - Clarifiers
 - Transfer points
- Storage tank vents
- Chemical plants

In these processes, the H₂S and oxygen from the gas stream are both absorbed and react according to



The reaction takes place in the liquid phase and it is very rapid. Absorption of H₂S into the aqueous phase is also rapid, particularly if the solution is kept in the alkaline pH range.

The oxygen absorption rate is not very good, however, and there are some tricky relationships that must be honored in dealing with aerobic unit design. For example, very low H₂S concentrations can be handled in scrubbers designed for any efficiency, but high H₂S concentrations require very high efficiency scrubbers.

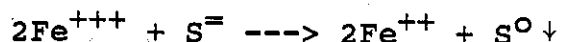
In the second case, the H₂S problem is associated with gas streams which do not contain any air and to which no air can be introduced.

The majority of the world's H₂S problems involve this type of gas source. Examples are:

- Refinery fuel gas
- Natural gas treating to meet pipeline specifications
- Amine acid gas treating for air pollution control
- CO₂ for beverage uses
- CO₂ enhanced oil recovery
- Shale oil retorting
- Coal gasification product

In these processes, the chemistry is more complex because usually the oxygen needed to oxidize the H₂S must be kept separate from the process gas. This means there are two vessels, an oxidizer and an absorber, and the solution circulates between them. Figure 1 is a sketch of the process flow for a LO-CAT(R) unit which works this way.⁴

In the absorber, the H₂S is absorbed and ionized and the iron reacts with it like this



The iron reduces very easily and the absorbers can be designed on the basis of the H₂S absorption rate alone. However, there must be enough oxidized iron circulated to the absorber to make sure there is at least enough to complete the reaction, or some of the iron will react according to



The chelating agents used commercially are strong enough to keep the iron from precipitating as $\text{Fe}(\text{OH})_3$ or $\text{Fe}(\text{OH})_2$, but they are not strong enough to keep FeS from precipitating.

The iron solution is then recirculated to the oxidizer where oxygen is absorbed and converts the iron back to the ferric form

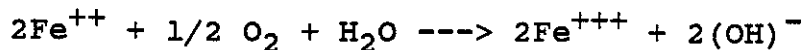
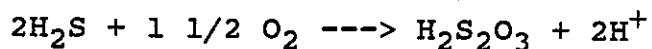


Figure 1 is a simplified flow diagram of an anaerobic LO-CAT(R) unit.

Again, the reaction between the iron and oxygen is very fast, so the oxidizer is sized for oxygen mass transfer alone. Oxidizers tend to be big because of the slow rate of absorption of O_2 into water.

There are some side reactions. Air acting non-catalytically with H_2S does this



and makes the solution get more acidic with time. KOH , NaOH , Na_2CO_3 , or ammonia can be added to keep the pH up.

Early Development⁵

For a process which appears so simple in concept, a great many practical problems arose in the early years.

The first chelated iron process was patented in the United States by Humphreys and Glasgow of London, England in 1962. This is indicated as the first milestone in the Chelated Iron Process (CIP) development charted in Table 1. The first commercial application was to refinery fuel gas. The process failed to work properly and was abandoned. ARI began the development of the LO-CAT process in 1972. Several of the CIP process shortcomings were corrected, including

1. Use of dual chelating agents - The CIP process used EDTA chelated iron. The EDTA works well at low pH (below 7) but loses its effectiveness as the pH increases.
2. The use of a low circulation rate and high Fe concentration for CIP makes it necessary to have a large pH change across the absorber. This was the problem that kept CIP from getting off the ground. If the pH of the solution was low enough to avoid $\text{Fe}(\text{OH})_3$ precipitation at the inlet, it was too low to absorb H_2S at the outlet. Or, if the pH was raised enough to absorb H_2S at the bottom of the absorber, it was too high at the top and $\text{Fe}(\text{OH})_3$ or FeS precipitated.

3. This was compounded by setting the circulation rate at exactly 100% of the theoretical iron. This just is not workable, because the oxidizer will not, under the best of circumstances, reoxidize the iron to 100% Fe^{+++} . There is an equilibrium between the $Fe^{+++}/(Fe^{++} + Fe^{+++})$ ratio and the level of dissolved oxygen in the solution. If the iron is not completely reoxidized, then less than 100% of the theoretical Fe^{+++} will be supplied to the absorber, and some iron will precipitate as FeS. This is effectively taken out of the solution as FeS reoxidizes slowly, so the solution is rapidly depleted of chelated iron and stops working altogether.

ARI began work on the LO-CAT(R) Hydrogen Sulfide Oxidation Process in 1971, without knowledge of the preceding work by H&G. The objective was to correct an emission problem at the Union Carbide Films and Packaging plant in Bedford Park, Illinois, which used the Xanthate process for making cellulosic sausage casings (similar to cellophane). H_2S was released at very low concentrations in a very large air stream.

The chelated iron approach was chosen because the chemicals were

1. Non-toxic
2. Inexpensive
3. Very effective

The CIP problems did not appear in LO-CAT because of some decisions made early on.

1. A dual chelate system was used, with EDTA as a "Type A" or low pH chelate, and sorbitol, a polyhydroxylated sugar, as a "Type B" or high pH chelate. This allowed freedom to operate at high pH, and avoided depleting the catalyst solution by precipitation of $Fe(OH)_3$. The Thompson patent application was filed in 1973 covering this development.
2. Low iron concentrations and high circulation rates were used to minimize the loss of catalyst components with solution discarded in the sulfur slurry.
3. 200% of the theoretical iron was provided in the absorber. This was to insure against FeS precipitation and minimize thiosulfate formation.

These changes made a workable process but aerobic applications were hard to find. A very small unit was installed on the vent air from a dissolved air floatation unit at Clark Oil and Refining Company in Blue Island, Illinois in 1974. After some months of successful operation, the LO-CAT process was announced at an AIChE annual meeting in 1975.

During this same period, Rhodia, Inc., now a part of Rhone-Poulenc, began working on an EDTA chelated iron process called CATABAN(TM), which was also aimed at aerobic H₂S removal systems. The CATABAN process suffered from the "single chelate" susceptibility to precipitate Fe(OH)₃ at high pH, but several novel schemes for contacting the solution and gas so as to avoid running short of Fe were incorporated in patents assigned to Rhone-Poulenc. CATABAN did not enjoy much commercial success, but one manufacturer of sulfonated cutting oils, D.A. Stuart Oil Co. did install a CATABAN unit which operated for a number of years. In 1983 this unit was converted to a LO-CAT(R) unit, and it is still in operation. ARI acquired Rhone-Poulenc's patent rights in 1983.⁶

During 1976 through 1980, a great deal of pilot test work was done in potential customer's plants and some licenses for some small units were sold:

Plateau Refining Co. - C₃/C₄ LPG product
Amax Metallurgical Labs - H₂S vent from Hydrometallurgy
reactor
Occidental Chemical - Phosphorus penta-sulfide plant effluent

Some of the problems inherent in the liquid phase oxidation to solid sulfur were uncovered in these plants. These included:

1. Difficulties in wetting the sulfur particles so that they would settle out of solution if
 - a. They were electrically charged
 - b. They got contaminated with oil

These were eliminated by application of surfactants and by minimizing oil contamination of plants.

2. Problems with sulfur plugging packings in absorber columns and piping. Usually related to item 1, but often avoided completely by good mechanical design.
3. Biological attack on the organic chelating agents. EDTA and sorbitol are edible, not only by people, but by all kinds of microorganisms. This has been eliminated by the use of ARI-400 Biochem(R), a patented and very effective biostat.

In 1980, two large oil refinery units were built and both started in 1981. These experienced some of the problems already described, but also identified two more that were not troublesome on small plants but are of critical importance on large ones.

1. Corrosion/erosion of carbon steel. This caused no trouble in the small plants, but led to replacement of some expensive components of the large plants with 304SS, and left us with a decided preference for stainless steel, plastics and plastic coated steel.

2. Type A chelate degradation. In small plants, a relatively large physical discard of catalyst solution along with the throwaway sulfur product concealed a substantial chemical loss of the Type A chelating agent. The large plants had no discard, so any catalyst addition represented chemical destruction of the catalyst.

The catalyst degradation problem was the most difficult one to overcome.

The problem was identified as breakdown of the Type A chelating material. While all organics are oxidized slowly in LO-CAT(R) plants, the EDTA-like materials have a unique mechanism for oxidation that involves the repeated change of valence of the iron.

The solution, "ARI-310 Catalytic Reagent" lay in the use of a different Type A chelate material, one which is stabilized to a considerable degree against oxidative degradation and capable of predictable operation. There is still some chemical consumption and this is likely to be the major operating cost in a large LO-CAT system. We are working on ways of reducing this cost still further, with some promising indications.

With the announcement of ARI-310 in 1983, chelated iron scrubbing began to come of age.^{7,8,9} Subsequent development has been rapid and diverse.

Figure 2 is a plot of the total number of units under license and total number of units successfully placed in service as a function of time, with some of the earlier milestones indicated. Figure 3 repeats this plot, but with the dollar value of the plants as the ordinate with estimated dollar value of the plants.

Figure 4 indicates the distribution of LO-CAT licenses among the various applications listed in Table 2.

Current Status

LO-CAT can take H_2S out of any gas or water stream with a few limitations -

- high temperature gases
- oily or tarry gases and liquids

and we are doing some work on both of these.

Current applications are shown in Table 2. While we are pleased to address just about any new application, there are several specific application areas which are worth special note because of the widespread occurrence of the problems, and the absence of references to LO-CAT as a solution in any previous publication.

- Sewage treatment plant ventilation air
- Landfill biogas treatment for power generation
- Crude oil tank loading system

Sewage treatment plants emit a variety of odorous materials, of which H₂S is usually the predominant one. A simple LO-CAT(R) unit removes practically all the H₂S, but may not get organic nitrogen or complex organic trace odorants. A carbon bed after a LO-CAT gives long life and freedom from odors. This is the state of the art for sewage cleanup. Pioneered by the City and County of Honolulu, the Sand Island LO-CAT plant, Figure 5, and three units at the Kailua WWTP have been in service for several months and perform well.

Biogas, generated by landfills and anerobic sludge digesters, is usable as fuel, but usually requires pretreatment prior to use to avoid air pollution and to protect the engine or turbine from corrosion. LO-CAT is ideal for these applications.

Unloading of crude oil into on-shore tank farms creates emissions of H₂S whenever sour oil is imported. North Slope, Arabian, Mexican and Venezuelan crude oils are all likely to have this problem. Not many installations of odor control equipment have been made. We have three such projects under way now.

Conclusion

Chelated iron scrubbing has come of age with the commercialization of the LO-CAT(R) Hydrogen Sulfide Oxidation Process. Characteristics of the system now in service are:

- They run well and have high efficiencies.
- They use dual chelation iron systems covered by the Thompson patents.
- They need surfactant additives.
- Biological control by ARI-400 Biochem.
- They need a stabilized catalyst system.

Some of the chelated iron processes proposed have omitted one or all of these requirements. LO-CAT is ready to meet the requirements of almost all H₂S removal jobs.

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⁵Hardison, L. C., "Application of the LO-CAT(R) Process to Sweetening Natural Gas", University of Oklahoma Gas Conditioning Conference, Norman, Oklahoma, March 5-7, 1984.

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⁸Annon., "Non-Toxic Catalytic Reagent Converts H₂S into Sulfur", Chemical Processing, Mid-November, 1984.

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TABLE 1

LO-CAT* DEVELOPMENT MILESTONES

<u>Year</u>	<u>Milestone</u>
1960	Humphreys & Glasgow Concept-Chelated Iron for H ₂ S Removal
1962	Hartley U.S. Patent Issued
1964	First CIP Process Plant Completed
1972	ARI Begins Laboratory Work on LO-CAT
1973-4	First LO-CAT Commercial Service
1975	LO-CAT Process Announced, AIChE Meeting, March 10-16, 1975
1978	Amax Plant Started
1980	Thompson U.S. Patents Issued
1981	Fletcher Oil Starts Up - First Large Plant
1983	Exxon Starts Up - First Natural Gas Application
1984	Tejas Startup - First Autocirculation Unit
1985	ARCO Startup - First CO ₂ Enhanced Oil Recovery Unit
1985	City of Honolulu -First Sewage Treatment Plant
1985	ONGC License Agreement - First Overseas Sale
1985	Thai Rayon Started - First Rayon Plant

*LO-CAT is a registered trademark for the ARI Hydrogen Sulfide Oxidation Process

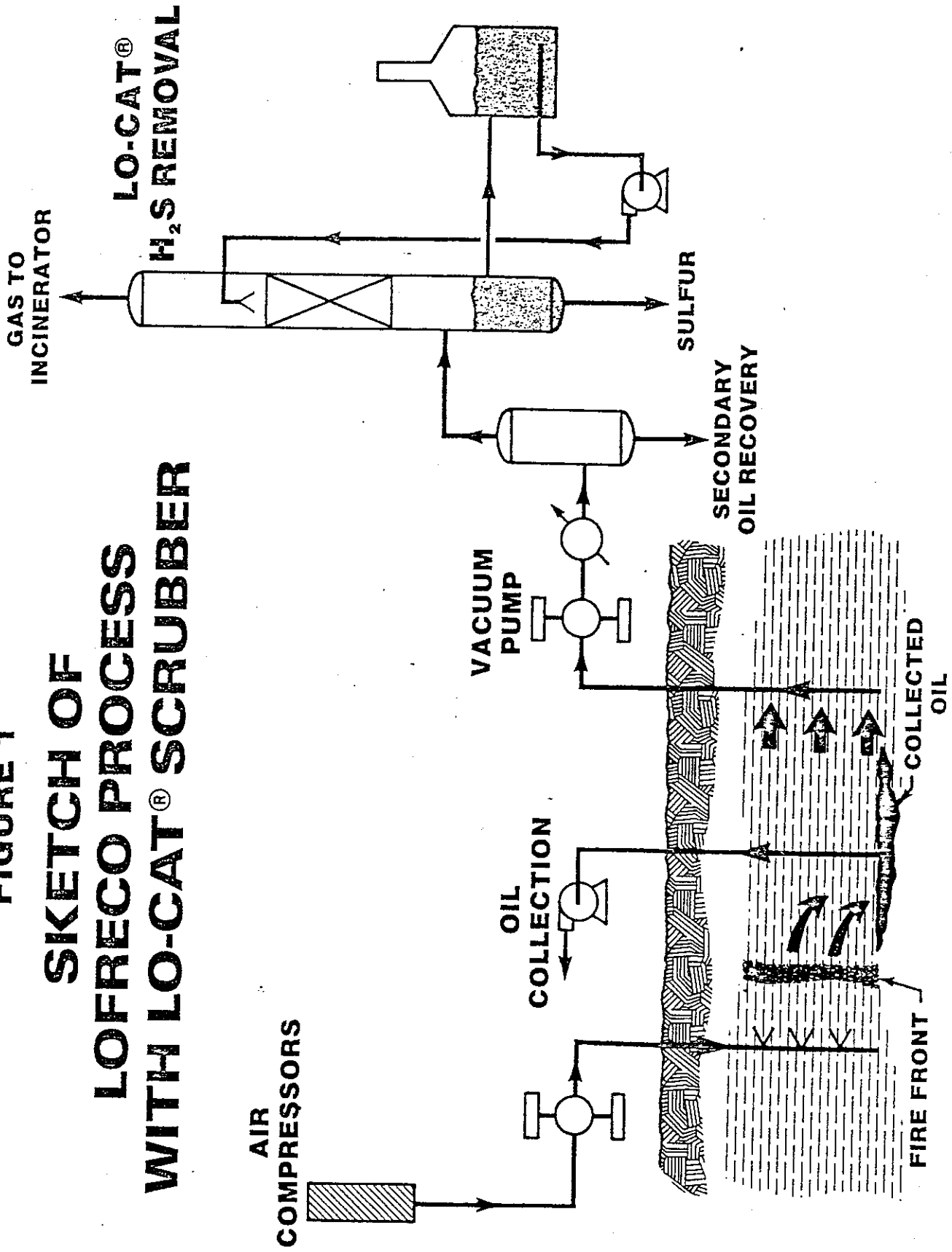
TABLE 2

CURRENT APPLICATIONS OF LO-CAT(R)
(Through December 31, 1985)

	<u>Units Under License</u>
Specialty Chemicals (SP CHEM) *	3
CO ₂ Sweetening (CO ₂)	6
Refinery Fuel Gas	2
Natural Gas Sweetening (NAT GAS)	4
Wastewater Treating Plants (WWTP VENTS)	4
Shale Oil Retort Gas (SHALE OIL)	1
Amine Acid Gas (AMINE ACID GAS)	13
CO ₂ Enhanced Oil Recovery (CO ₂ EOR)	4
Rayon Manufacture (RAYON)	1
Tank Vents (TANK VENTS)	<u>3</u>
	41

*Names in parentheses correspond to graph in Figure 4.

FIGURE 1
SKETCH OF
LOFRECO PROCESS
WITH LO-CAT® SCRUBBER



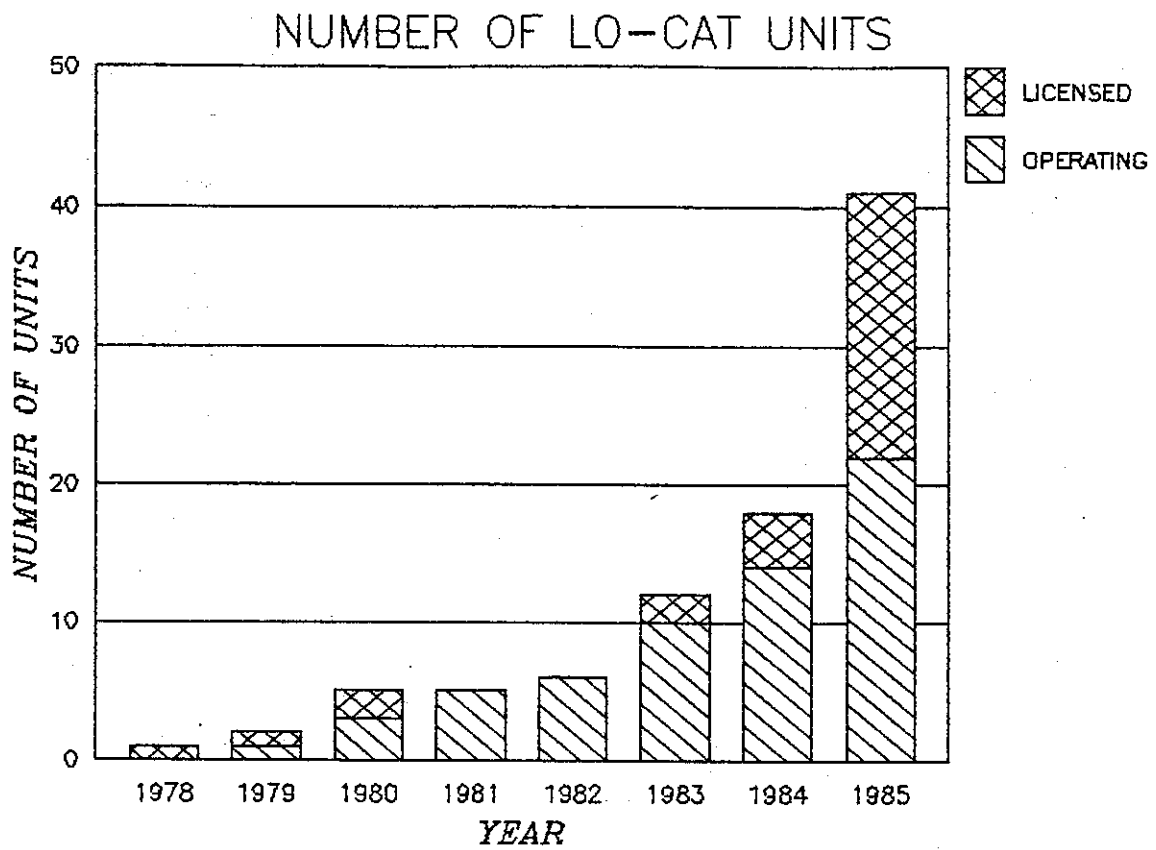


FIGURE 2
 Number of LO-CAT Units -
 Under License and Started Up

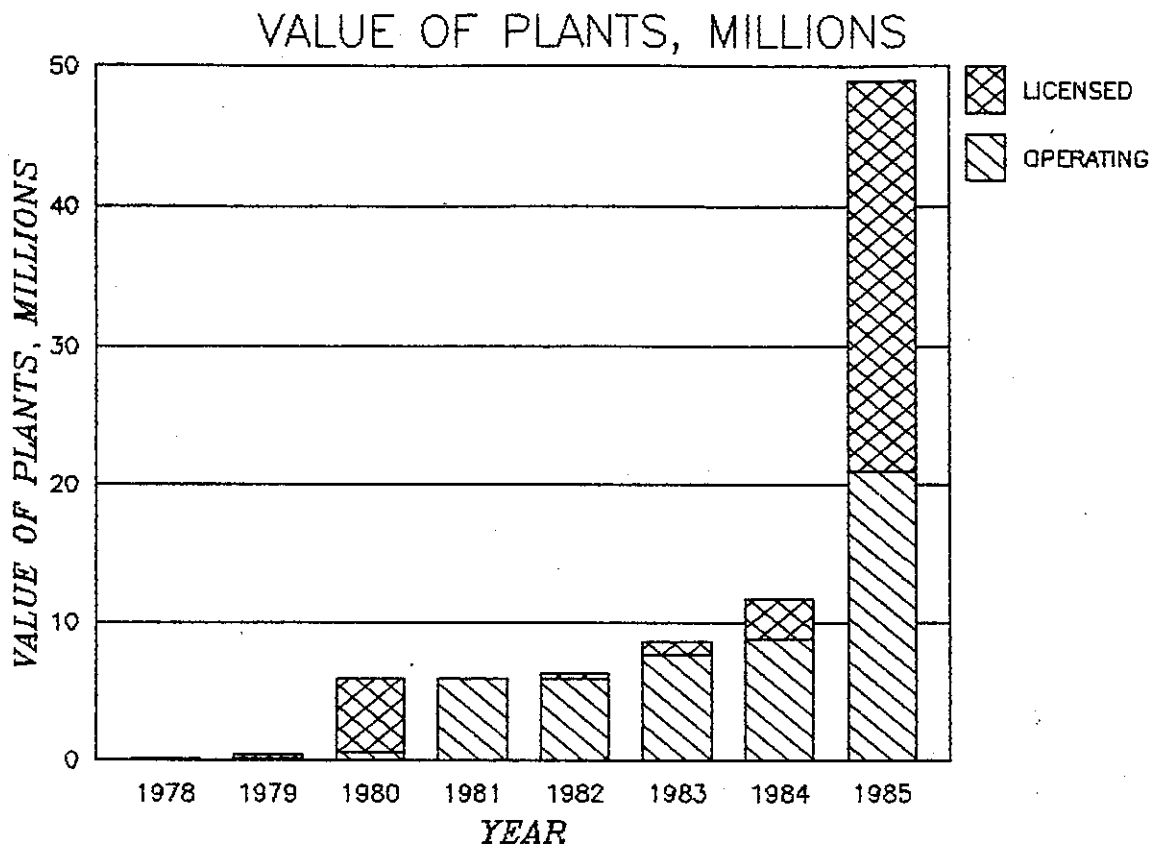


FIGURE 3
Value of Plants -
Under License and Started Up

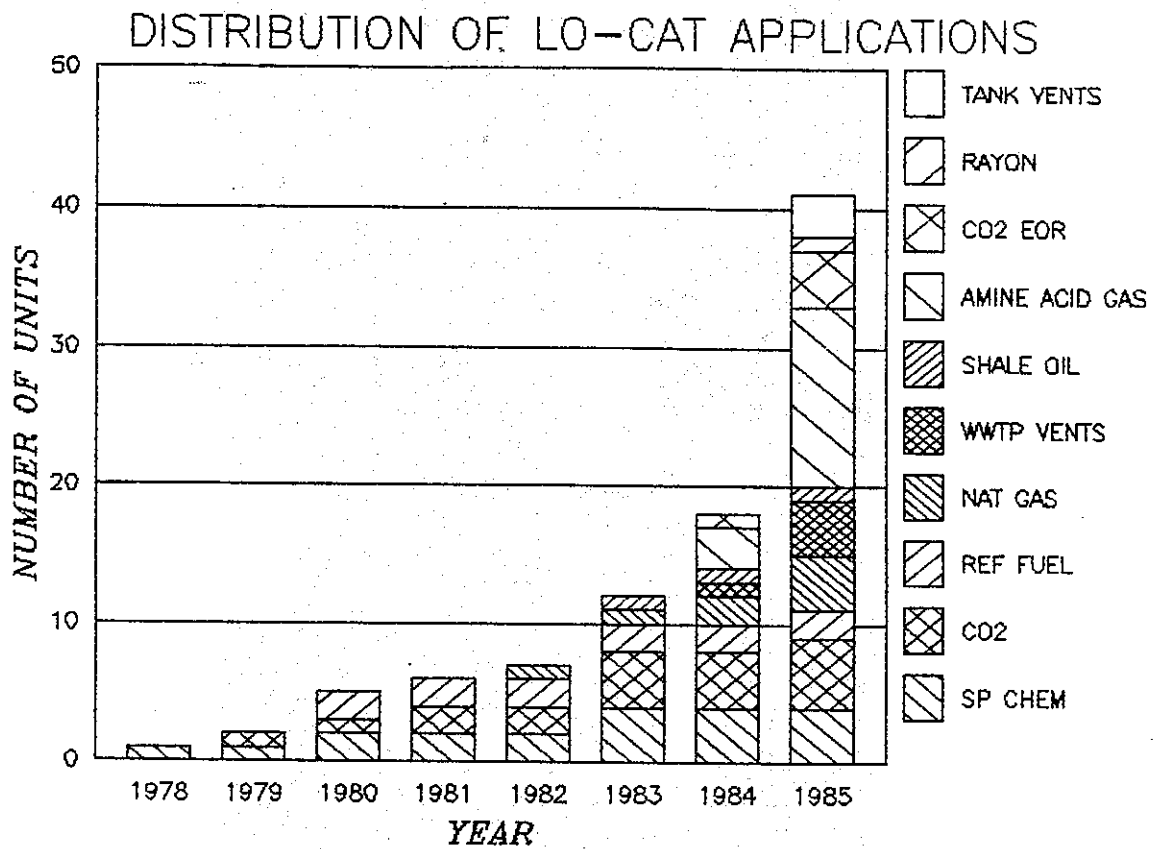


FIGURE 4
 Distribution of Licensed
 Plants by Application

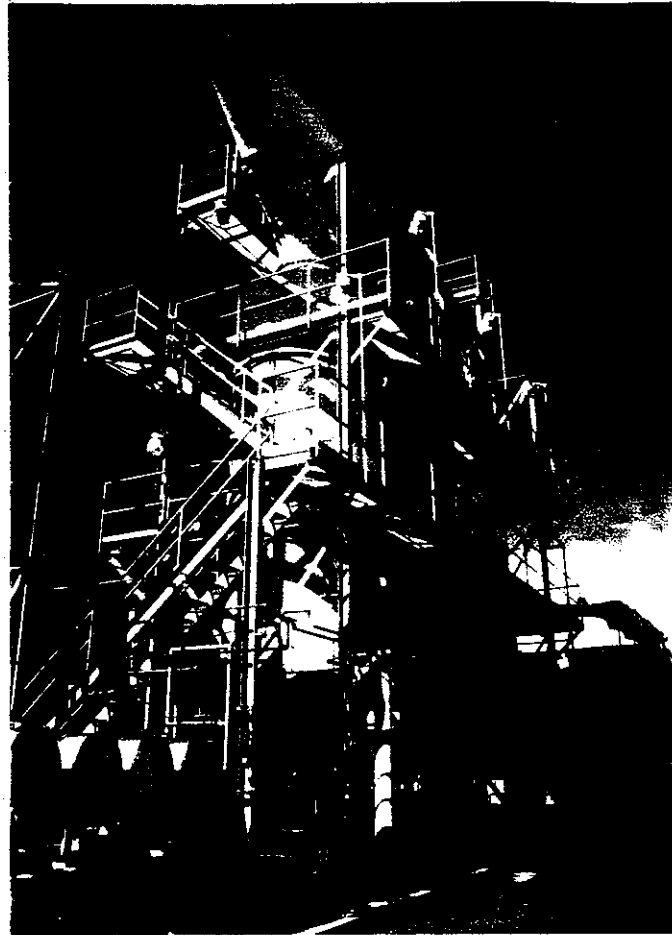


FIGURE 5

Photograph of Sand Island WWTP
LO-CAT Installation
(Honolulu, Hawaii)