Progress in Smog Control

by A. J. Haagen-Smit

Since the war, the influx of people to California has been one of the greatest mass migrations in history. Today, some 200,000 people settle in the Los Angeles area per year. This explosive growth is not always an undivided pleasure when orange groves rapidly disappear to make room for real estate developments and transportation facilities begin to fail in their task of moving people to and from work. During the past ten years another unpleasant discovery was made when we began to notice that something was the matter with our supply of air.

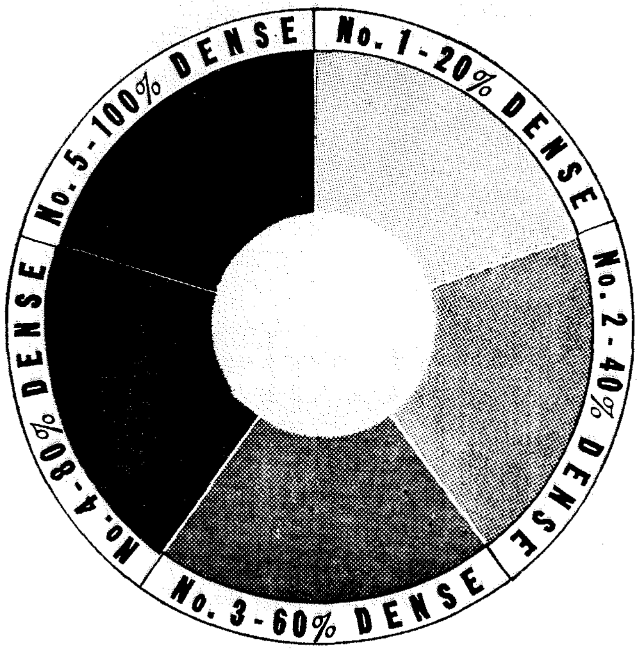
We may tolerate considerable self-made air pollution in our homes and in buildings where we gather daily, but when the outside air becomes polluted the telephone exchanges in the police and fire departments and the Air Pollution Control District are swamped with calls. This happened a few times when Pasadena residents were surprised at night by a strong odor of mercaptans. While somewhat unpleasant, and objectionable from an esthetic point of view, this type of pollution is rather harmless, and is limited to areas close to the source. A more serious situation developed during the war years when an eye-irritating wave of pollution moved across the valley. Its origin was soon located and found to be a synthetic rubber plant. After suitable measures were taken to eliminate air pollution from this source, the symptoms disappeared, and the excitement died down.

A few years later, the population of this area was again disagreeably surprised by foreign odors and eye irritation. This time it wasn't easy to find the culprit, and numerous committees were formed to demand action. This resulted in the formation of an Air Pollution Control District, in 1948, under an enabling act which authorized the Board of Supervisors of Los Angeles County to act as an Air Pollution Control Board in the County of Los Angeles. At the present time, similar control districts have been set up in the adjacent counties of Orange, Riverside and San Bernardino. A close cooperation between these districts is, of course, necessary, for air pollution does not recognize any city or other administrative limits.

The Los Angeles County Air Pollution Control District has recently celebrated its 10th anniversary. During this time, under the able directorships of Dr. Louis C. McCabe, Mr. Gordon P. Larson and the present director, Mr. S. Smith Griswold, much progress has been made in abolishing the sources of visible smoke, as well as sulfur dioxide.

It is perhaps typical of the early period of smog control that the District employees gave the name, "Ringelmann Club" to their newly-formed employees organization. The name "Ringelmann" is intimately connected with degrees of smoke density. Ringelmann invented a chart indicating by five equal steps between white and black, varying shades of gray to which smoke plumes could be compared.

Although not the official chart, a handy observation card (see page 6) illustrates the principle used in smoke measurement. Most air pollution authorities who use the card agree that the real measure of objectionable stack emissions has to be indicated by weight of dust per unit as well as the distribution of the particles according to size. This is even more true of non-black plumes, such as steam or aerosol types from condensations of vaporous materials, which are dependent on factors such as wind, humidity, temperature, cloud background and others.



The Ringelmann chart is used to determine whether emissions of smoke are within legal limits or standards of permissibility. The card shown here, adapted from the official Ringelmann chart, has a viewing hole in its center, and is frequently used for quick reference.

In this early period many important emissions were controlled. These include the effluents from two large steel mills, some 120 foundries and open burning dumps. Also, while the control program was under way, research was carried out which established that the eye irritation and typical plant damage, as well as the odor observed during smog attacks, were due to a photochemical oxidation of organic material, mostly hydrocarbons, in the presence of oxides of nitrogen.

The acceptance of these findings led to a drastic control of hydrocarbon emissions at the refineries. Oil-water separating tanks were covered, open-vented tanks were converted to closed systems, and the general supervision of air pollution problems in the petroleum industry is now well taken care of, day and night, by specially appointed personnel responsible directly to the refinery manager.

With the considerable reduction in the refinery hydrocarbon emission, attention was directed to the major smog source—the automobile. Studies were initiated on the exhaust gases of the automobile—a phase of engine studies which had received practically no attention in the past. Both in Detroit and in Los Angeles the surprising discovery was made that the automobile engine is not as efficient as its smooth performance might lead one to believe. Seven to eight per cent of its fuel leaves the exhaust incompletely burned.

The study of the operation of the automobile has shown that most of the hydrocarbons are released during acceleration and deceleration. Devices are being developed which shut off the flow of gasoline during deceleration, when no power is required anyway, and much work is being done on after-burners of different types. Some work with a catalyst bed; others utilize a spark plug to ignite the gases before they leave the exhaust.

The most desirable way of controlling the hydrocarbon losses would be to have a more complete combustion in the engine itself, but we may have to wait for the introduction of the turbine engine to passenger cars —a matter of at least ten years. Others are seeking a cure by modification of the fuel. At present, opinions are divided on the effectiveness of such a change, and research is under way to resolve these differences.

It is clear that the development of a satisfactory control device for the automobile emission is many years away. The Air Pollution Control District, primarily an organization charged with enforcing the law with regard to objectionable emissions, has stimulated a great deal of engineering research and development work of this type, but it could not very well be expected to take over the task of the automobile industry to meet this challenge. During this waiting period, the District has started with renewed vigor to give attention to sources other than the automobile.

Under the efficient guidance of Captain Louis J. Fuller, formerly of the Los Angeles Police Department, some 40 inspectors are roaming the 400-mile-square Los Angeles area. Their cars are equipped with two-way radio, and they are at all times in touch with headquarters and can investigate reports of objectionable emissions in the matter of a few minutes. Aerial observation, integrated with this system, facilitates their work. As a result, the number of violations cited during the past three years was about 11,000, compared to 700 for all the eight previous years of the District's existence. The nature of the violation varies from the smoking automobile to stacks of industrial operations.

Now that private backyard incinerators have been banned, there are relatively few sources of smoke left. Among these are some municipal incinerators, the Hyperion sewage disposal plant, and most of the municipal and privately owned power plants—which include those of industry, as well as those of utility companies.

In almost all of these cases the quantities by weight of dust or chemicals leaving the stacks are well within the limits prescribed by law. Nevertheless, the opacity of the smoke plume is greater than that designated as permissible on the basis of the Ringelmann chart.

For example, a typical analysis of the stack emission from one of the large oil-burning plants (capacity, 350,000 kw) shows a stack gas concentration of 1,000 parts per million of sulfur dioxide, while 2,000 ppm is the legal limit. The dust load is 0.05 grains per standard cubic foot, as compared to the legal limit of 0.3 gr./scf. or 770 lbs./hr., calculated to 12 percent CO_2 at standard conditions (60° F., 14.7 lbs./sq.in. absolute). The capacity, on the other hand, varies from 20 to 100 percent, depending on weather conditions, while 40 percent is considered a violation.

On the basis of previous experience with oil-burning plants, the Air Pollution Control District had not much choice in denying the Southern California Edison Company a permit to operate its newly erected El Segundo steam station, although it was built according to specifications approved by the Control District. While a solution could have been found by abandoning the burning of fuel oil, the always rather critical fuel supply made this impossible.

The difficulty in keeping up with the demand of the growing population for more fuel is also felt in the necessary construction of electric generating stations. Every new plant gives a respite of only a few years, and presently new units are being built or are on the drawing board to follow the upswing in electrical demand. It is clear that this building and operating schedule cannot be interrupted without serious consequences for the community. This embarrassing situation was solved by the Air Pollution Hearing Board, a judicial body created by the Governor of California to arbitrate matters of air pollution.

This board, consisting of three members—our own R. L. Daugherty, emeritus professor of mechanical and hydraulic engineering, together with Mr. William A. Sherwin and Mr. Delmas R. Richmond, both representatives of the legal profession—permitted the Southern California Edison Company to operate under a variance with the proviso that an investigation be made to determine the possibility of reducing the opacity of the plume. The scope of the research program instituted by the Edison Company was considerably broader than just reducing the opacity of the plume to the legal limits, and has considered the emission of dust, and of oxides of sulfur and nitrogen, as well.

These investigations, and those conducted by other power-generating organizations in this area, are of much more than local importance, and have a direct bearing on similar problems in other parts of the country. Combustion of various kinds, whether in automobiles or in industrial furnaces, is by far the largest chemical operation, and is responsible for most of the air pollution problems.

The amount of fuel burned in the United States is tremendous. The total energy produced from all fuels and water power is on the order of 100 quadrillion Btu's, or 300 trillion kilowatt hours per year. (It is difficult to imagine what such a figure represents in comparison to a man's energy expenditures of approximately ½ kwh per day.)

In the area of southern California, approximately 3 to 4 percent of this total energy is produced in the burning of local oil supplies and natural gas. In addition, huge dams, such as Hoover Dam, which supply hydropower to areas some 400 miles away, have been built. Even today this development continues, and one of the most interesting modern hydropower systems is in our own backyard—the Big Creek water power project of the Southern California Edison Company.

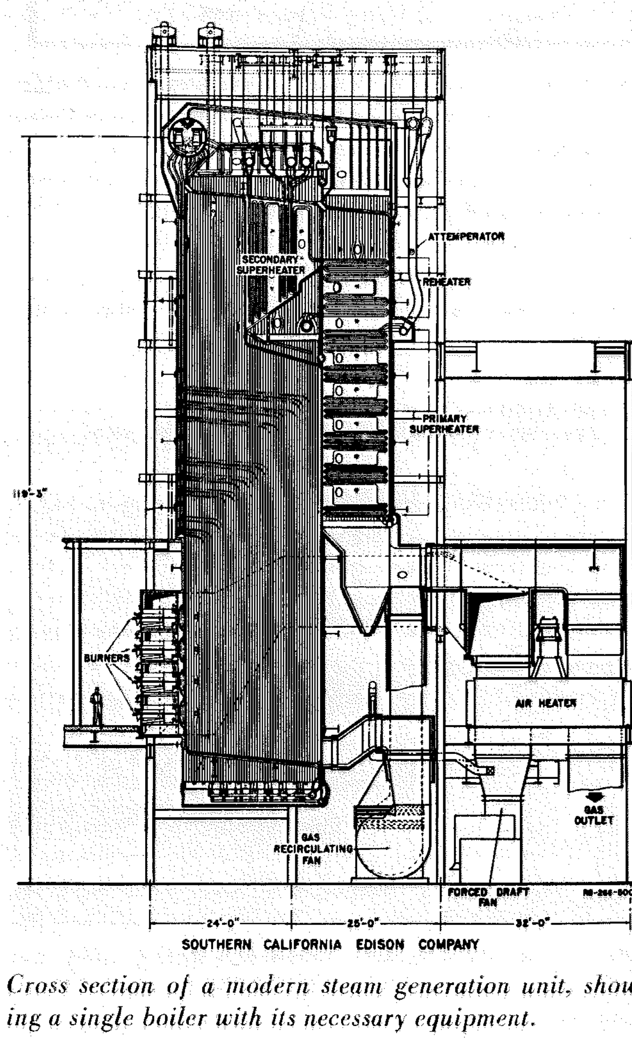
Through a succession of dams interconnected with miles of tunnels, the water of the San Joaquin River is reused several times to produce electrical power before it is finally distributed as irrigation water. In this process it has generated 500,000 kw of electricity. With the energy derived from Hoover Dam, the hydropower represents about 25 percent of the total energy need of this area.

Unfortunately, this cleanest source of power is limited, and the rest has to be supplied by combustion of fossil fuels, oil and gas. The gas is burned in kitchens and household furnaces, and in the production of electric power. The utilization of oil is much more complex. It is converted at high temperatures in hydrogenation and reforming processes to gasoline and other petroleum products, and the residual oil is used for power production. The daily consumption of these different fuels is as follows:

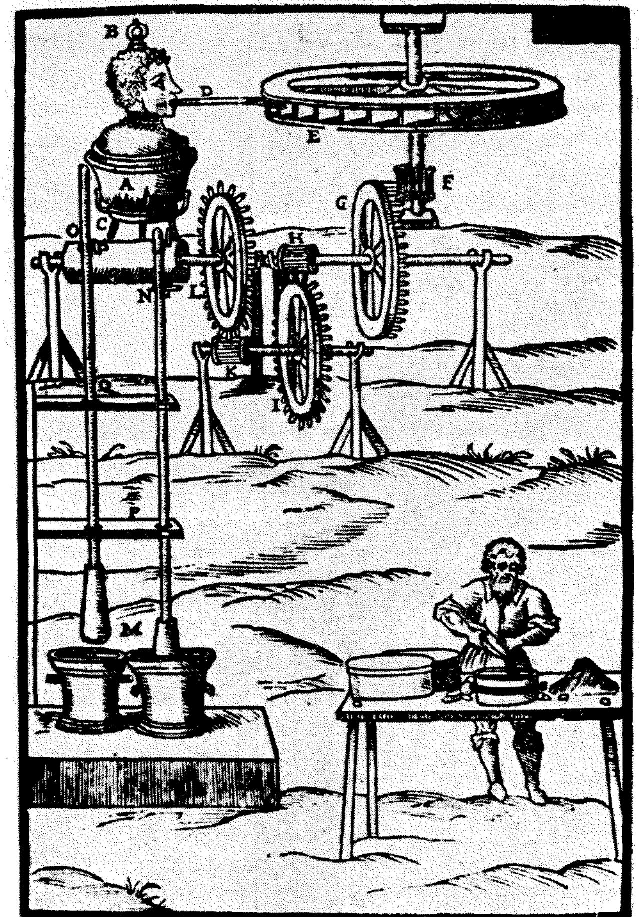
Daily Fuel Consumption in the Los Angeles Area

	Quantity	*Equivalent Bbls. of Oil*
Gasoline	5,500,000 gallons	110,000
Oil	65,000 barrels	65,000
Gas	1,000,000,000 cubic feet	167,000
Hydropower	891,000 kw	30,000

All hydropower is converted into electricity and, in addition, 3,000,000 kw are produced in oil and gas burning, chiefly by the Southern California Edison Company



Cross section of a modern steam generation unit, showing a single boiler with its necessary equipment.



The modern process of power production doesn't differ much from one of the first simple steam engines, illustrated above, developed after an idea of Leonardo da Vinci. In both cases, the force of expanding steam is converted into mechanical energy.

and the cities of Los Angeles, Pasadena, Burbank and Glendale.

The El Segundo steam station, where most of the Edison Company's air pollution research is conducted, accounts for 350,000 kw—or about 1/12 of the total production in this area. To produce this much electricity, equivalent to one-half million horsepower, 12,000 barrels of fuel oil are consumed per day. When gas is available, three million cubic feet per hour are burned in the two units.

One must visit such a plant to really grasp the magnitude of these operations and the tremendous power developed. In principal, the process of power production is quite simple, and doesn't differ much from one of the first steam engines (illustrated above) developed after an idea of Leonardo da Vinci.

Essentially, we have a boiler producing steam, which turns a turbine. The process has become more complicated, however, as attempts have been made over the years to increase the efficiency. This is one reason why the temperature of the steam is raised to 1,000° F (538° C.) and the pressure as high as 2,000 lbs./sq. in. (136 atmospheres).

This operating steam temperature is continuing to rise at the rate of about 12° F. per year, and is expected to reach 1,400° F. in 1980. The same is true for the pressure, which is doubled about every 12 years, and should by 1980 be in the order of 7,000 pounds per sq. in. absolute.

Boiler tubes and turbine blades have to withstand the action of this nearly red-hot water and steam. Much engineering research went into this problem before the efficiency of today was obtained—and the efficiency is still going up.

The power plant engineer is an expert in obtaining the maximum efficiency in the combustion of his fuel, and tests of the stack gases reveal the virtual absence of hydrocarbons and carbon monoxide. This is in sharp contrast to the automobile performance, where the CO concentration amounts to several thousand parts per million (0 - 3.6%). Unfortunately, the oil, because of its origin from living organisms, contains ash and sulfur. The ash contains an appreciable proportion of vanadium, nickel and iron. It is generally held that this vanadium has come from fossil marine organisms. Even at the present time we find some sea animals such as *Ciona*, the sea squirt, and certain *ascidia*, with a vanadium content of ½ to 1 gram per kilogram dry weight. Nickel is a common though minor constituent of plants and animals.

Compared to other dusty operations, the amount of solids coming from an oil-fired burner is a hundred times smaller.

In most dusty operations, the escaping materials are rather coarse, and the particle size ranges from several microns to big cinders. Settling chambers, baghouses and cyclones are now extensively used in sawmills, foundries and incinerators. Unfortunately, these do not take care of ultrafine dust, such as that produced in the burning of oil. The particle size of this ash is in the order of 0.5 - 2 microns, and its behavior is more like that of cigarette smoke.

Quite effective in this small particle field is the electrostatic precipitator. In this device, a charged particle passing through an electric field will be attracted to one of the electrodes. The electrodes are usually in the form of plates or tubes, and on these the dust will accumulate. It can be easily removed in simple mechanical fashion, such as rapping or purging with a blast of air. While the particle is travelling at high speed through the precipitator, its sideways motion towards the plates takes many seconds. For this reason a high voltage, from 15,000 to 40,000 volts is used to speed up this movement.

At the El Segundo steam station, 350,000 cubic feet of gas leaves the stack every minute, carrying with it 1.5 lbs. of dust. The removal of this extremely small quantity must take place in a very short time, because every minute one is faced with the assignment of processing a new batch of 350,000 cubic feet of gas.

The lack of previous experience on the application of precipitators to oil-burning power plants required the building of pilot precipitators. To make intelligent decisions in the extrapolation to a large-scale boiler, the pilot installations were quite large—with capacities for handling 1/50 and 1/200 of the total effluent.

After extensive testing, the conclusion was reached that the plume is largely due to dust, and only during exceptional periods of unfavorable weather does the sulfuric acid play an important role. In the 350,000 cu. ft./min. of effluent gas from one unit, only 2 ounces of dust will remain after passage through the precipitator, which means a collection efficiency of greater than 90 percent. The removal of dust also results in some removal of sulfuric acid, assuring an additional safety factor.

The electrostatic precipitator to be installed by the Southern California Edison Company has been designed in such a way that even the slowest particles most responsible for the plume will reach the collecting plates while they are passing through the system. This, of course, requires a long path, and makes the collection apparatus quite large and expensive. The full-scale unit which will be built this year will measure about 100 feet long, 30 feet high and 34 feet wide. With this large chamber, approximately 20 seconds will be required for the passage of 350,000 cu. ft. of gas.

The material collected is quite corrosive, and extensive experiments have been carried out on the addition of neutralizing reagents such as dolomite and ammonia. The removal of the acid lowers the condensation point and it is now possible to consider the release of the stack gases at a temperature lower than the present 300° F. A further study of this potential heat is in progress.

In our control efforts the oxides of sulfur and nitrogen have to be considered. The oxides of sulfur have always stood in bad repute, and consequently conditions in other industrial areas are often extrapolated to the Los Angeles area without any real basis. Sulfur dioxide does not irritate the eyes at concentrations observed in our atmosphere (from 0.0 - 0.20 ppm) and its concentration is about 100 to 200 times less than the threshold limit value of 10 ppm adopted by industrial hygienists.

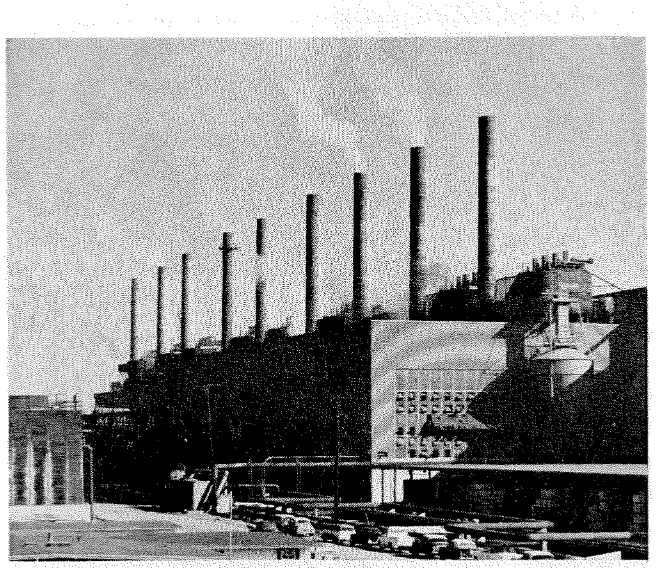
No plant damage attributable to sulfur dioxide has been found in recent years since oil refineries and sulfuric acid manufacturing plants have adopted recovery processes for most of the sulfur previously released into the air.

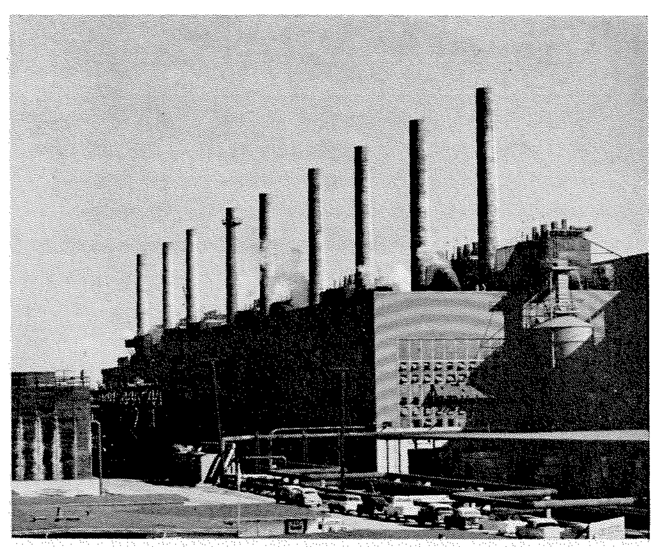
Sulfur dioxide control merits consideration from a long range point of view since the expansion of industry will gradually raise the SO_2 level. Also, from a public relations standpoint, it is expedient to give attention to a possible reduction of sulfur dioxide. For this reason, experiments have been conducted with the object of checking the economic feasibility of reducing the SO_2 content of the flue gas. The low concentration of SO_2 in stack gases, in the order of 1,000 ppm, makes recovery extremely difficult and expensive.

The Bureau of Mines has considered some 60 means of removing SO_2 from flue gas. Only a few seem to warrant laboratory investigation. In our research efforts we have added two more processes. One consists of an adsorption process and subsequent release of SO_2. The other manufactures concentrated sulfuric acid by passing the flue gas over a vanadium catalyst. The latter process, especially, has some appeal, since the dust itself contains large quantities of vanadium.

These processes have been carried out far enough to enable a reasonable engineering estimate to be made of the cost of a full scale installation. The cheapest and simplest process, which consists of scrubbing with water and subsequent neutralization of the water washings, costs $3,000,000 for one unit, and in addition, $1,000,000 per year for its operation and maintenance.

The results obtained are undesirable because a new





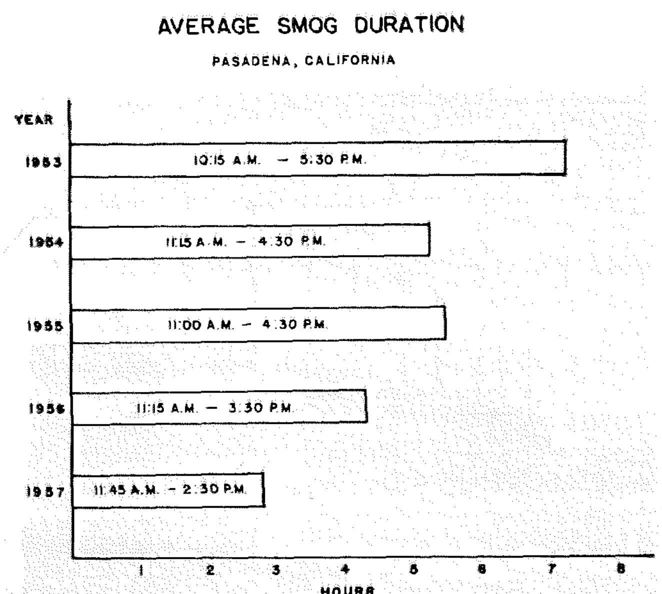
These two pictures of the Kaiser Steel Company plant in Fontana, taken within minutes of each other, demonstrate the effectiveness of smog control. The picture at the left was taken with all the smoke-control units temporarily shut off. At the right, just minutes later, the equipment is back in operation against a clear sky.

problem of disposing of the tremendous quantities of salts formed is created. When chemical manipulations such as catalytic conversion or adsorption are added to the scrubbing process, the price increases considerably. For example, a process using ozone plus manganese chloride will cost initially more than the construction of the entire power plant, and in addition, \$3 - 4,000,000 per year to operate. Any hope that the process would pay for itself evaporates when it is realized that the Edison Company could sell sulfuric acid made from stack gas at \$175/ton to compete with the usual price of \$22/ton.

The idea of removing sulfur, as well as metals, from the oil before it is burned seems quite attractive. After all, we have in that case to deal with only 6,000 barrels per unit, or with a volume of approximately 25,000 cubic feet per day, as compared to half a billion cubic feet per day of stack effluent. Unfortunately, both metals and sulfur form an integral part of the constitution of the oil, and simple washing, unpleasant as it may be, is not going to remove either one of these components. For a successful removal, the oil has to be cracked and hydrogenated at higher temperatures. The total cost of this process which, by the way, is not yet available, has been estimated to add approximately one dollar per barrel of fuel, which raises the annual fuel cost by about \$2,000,000.

Economic conditions would have to change considerably, and also the arguments for the control of oxides of sulfur in this area would have to be more convincing before serious thought can be given to adding the cost of the removal of SO_2 from flue gas, to the existing production costs.

A more healthy solution for both dust and sulfur problems in populated areas is the use of natural gas,



The result of air pollution control measures can be seen by the decrease in the average duration of smog in Pasadena over the past few years, in spite of a constantly increasing population.

which contains practically no mineral or sulfur compounds, and hence can form no dust or oxides of sulfur. The Edison Company has been diligent in obtaining the maximum amount of gas. Research has made it quite clear that in highly populated areas the burning of gas is the best remedy for air pollution nuisances, even though it must be transported from sources as distant as Mexico or Texas.

Up to this point we have discussed only those ingredients of the flue gas which might lead to the formation of haze. Although this is one of the aspects of Los Angeles smog, neither oxides of sulfur or dust could possibly be held responsible for the eye irritation and plant damage typical of Los Angeles smog, or the intense rubber cracking observed during smog periods.

As mentioned earlier, it has been well established by now that these effects are due to the oxidation of organic material under the influence of sunlight. In this reaction the oxides of nitrogen play a dominant role. Their origin is in a fixation of atmospheric nitrogen and oxygen during high temperature combustions in automobile engines and in burning of gas and oil. Stack gas from power plants contains from 300 - 700 ppm of oxides of nitrogen. This means that, per 175,000 kw unit, 10 - 15 tons of oxides of nitrogen are produced daily. The total amount produced in the Los Angeles basin is estimated to be about 600 - 700 tons per day.

Many attempts have been made to reverse the reaction by which oxides of nitrogen are formed, by trying to split the compound back to its original components— harmless nitrogen and oxygen. For this purpose some 40 different catalysts were tested without significant success. We have to realize that even when a catalyst is found, it would be necessary to apply engineering methods similar to those used for the removal of oxides of sulfur, and any one of those processes would turn out to be quite expensive.

Since the formation of the oxides of nitrogen is highly dependent on the temperature, any reduction in the combustion temperature would lead to a reduction in the oxides of nitrogen. Here a conflict of interests develops between those who would like to see the furnace as hot as possible, and the air pollution experts who would like to see it as cold as possible. In a systematic study of burning conditions, several ways have new been found to reduce the temperature without too severe a curtailment of efficiency. Joint studies with engineers of the Babcock and Wilcox Company are now under way on a two-step burning of the incoming fuel oil. The intake air is reduced at the burner site, and an equivalent amount is introduced through the rear wall of the furnace. Four large ports have been constructed along the upper wall of the firebox, and dampers permit the regulation of the air admitted.

Although these full-scale experiments are still in the initial stages, it has already been shown that predictions based on preliminary work were correct. The infrared analyzer monitoring the concentration of nitric oxide (NO) in the flue gas registered a decrease of approximately 25 percent. This reduction, if applicable to other oil and gas burning installations, would be equivalent to a reduction of 75 tons of nitrogen oxides per day in the whole basin.

Similar studies on automobiles and diesel engines should lead to a substantial reduction in NO emissions from these sources.

The air pollution control work by the Edison Company has been accomplished with the cooperation of several agencies—the Bechtel Corporation, Truesdail Laboratories, Standard Oil Company of California, Babcock and Wilcox and others. The technical skills and knowledge of all power-generating organizations in this area, as well as the air pollution control districts of San Bernardino, Orange and Los Angeles Counties have been made available through the formation of a Joint Research Council. Its regular meetings have been a forum of discussion on any progress made.

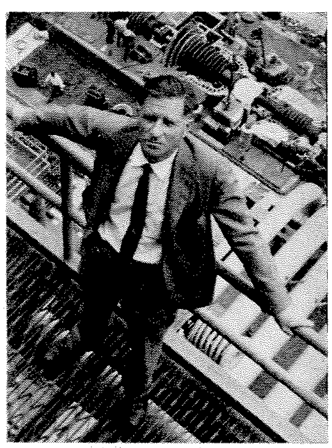
The Edison Company's decision to change its program from one of research to that of predominantly engineering by building a full-scale electrostatic precipitator and executing the recommendations based on the research findings is a most significant step towards ultimate control of Los Angeles smog, for it points the way for reduction of power stack emissions in general, of privately owned as well as municipal plants.

When, in addition, the plumes of city-owned incinerators have disappeared, the problem of the automobile will stand out even more clearly. The nature of this problem and the cures which are needed are such that they require that all industrial sources be under control before we can think of attaching hundred dollar mufflers to three million automobiles.

In the meantime, we are enjoying improved smog conditions which can only be attributed in part to the favorable weather. The oxidant, the typical manifestation of Los Angeles smog, is decreasing on the average, both in maxima reached and in duration. When the smog rolls in now, its duration is a few hours, compared to daylong sieges a few years ago; rubber cracking and dustfall values have decreased, and visibility has improved.

It is not possible to point to the control of one source as the cause of this improvement. Air pollution control in a complex area can be achieved only by the tenacious, step-by-step control of numerous sources. There is no magic wand.

About the author



Arie Jan Haagen-Smit, professor of bio-organic chemistry at Caltech, is a native of Utrecht in the Netherlands. After receiving his PhD from the University of Utrecht in 1929 he taught chemistry there until 1936, when he was appointed to Harvard University as an instructor in chemistry. The following year he came to Caltech as an associate professor of bio-organic chemistry and became a full professor in 1940.

Although Dr. Haagen-Smit's name is now synonymous with smog research, he's known internationally for his work in flavor chemistry and the isolation and structure determination of various plant substances as well as investigations of food flavors, wine and milk. Applying the technique he had developed for flavor studies, he was able to identify smog in his laboratory in 1949.

In 1950 Dr. Haagen-Smit was granted a leave of absence from Caltech to direct full-time research on smog for the Los Angeles County Air Pollution Control District. During this time, he discovered a new type of modern air pollution formed from the photochemical oxidation of hydrocarbons in the presence of sunlight and oxides of nitrogen.

In 1956 Dr. Haagen-Smit received another leave of absence to serve as director of research for the Southern California Edison Company. His work there has been concerned with curbing the effluents from stacks on central power stations. By determining the composition of the effluents, he has been able to learn about their contribution to smog and has developed corrective processes. His specially-designed equipment has been used successfully at Edison's El Segundo and Etiwanda plants. Much of the work he has been doing there is described in the accompanying article.

On May 27 Dr. Haagen-Smit was awarded the 1958 Frank A. Chambers Award by the Air Pollution Control Association, an international smoke-control organization. In 1957 he won the Los Angeles County Clean Air Award.

This year two other Caltech professors received the Clean Air Award—Royal W. Sorensen, emeritus professor of electrical engineering, in recognition of his outstanding services in the pioneering and the application of electrostatic precipitators and the control of particulate emissions in industry; and Frits W. Went, professor of plant physiology, for his research in Caltech's Earhart Laboratory which has established a connection between air pollution and plant damage.