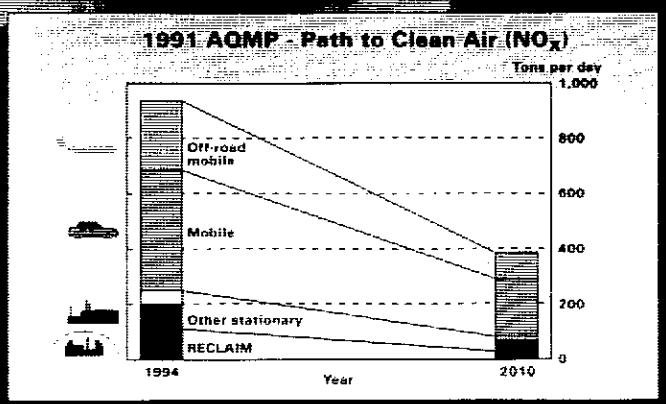
RECLAIM drives analytical monitoring upgrades

Chevron's El Segundo refinery spent $20 million upgrading systems to meet new air pollution control requirements.

To meet the strict air pollution control requirements in the Los Angeles Basin imposed by the South Coast Air Quality Management District (SCAQMD) for the Regional Clean Air Incentives Market (RECLAIM), Chevron's El Segundo refinery spent more than $20 million. The money was spent installing new and upgrading old monitoring equipment; no new emission reduction equipment was required. Twenty-eight new analyzer systems were installed, seven of nine existing analyzer systems were upgraded, and programmable logic controllers (PLCs) and computers were installed to bring the analyzer data and other measurements together for analysis.

The Los Angeles Basin has been a nonattainment area for ozone, carbon monoxide, and particulate matter less than 10 microns in size (PM_{10}) for many years. Thus, the level of these emissions has been scrutinized closely, and the SCAQMD was looking for a new way to control emissions. "Command and control" rules, which require each source to take incremental steps to reduce emissions within a specified time frame, have been used since the U.S. Environmental Protection Agency (EPA) was created. When the EPA amended the Clean Air Act in 1990 to reduce sulfur dioxide (SO_2) emissions from the power industry in what is commonly referred to as the "Acid Rain Rule," trading emissions credits based on SO_2 reductions below the targeted level was allowed. Power plants could purchase these credits to bring their emissions below the designated threshold values.

Taking its cue from the Acid Rain Rule, the SCAQMD began working on the proposed RECLAIM rule in 1990. Through the standard process of rule proposal, public comment, and response, the rule evolved until it was promulgated in October 1993. Similar to the Acid Rain Rule, it required each source to reduce SO_2 emissions on an annual, facility-wide basis. Unlike the Acid Rain Rule, it also included similar reduction requirements for nitrogen oxides (NO_x). Emissions percentages for SO_2 and NO_x by source category are shown in Figure 1.



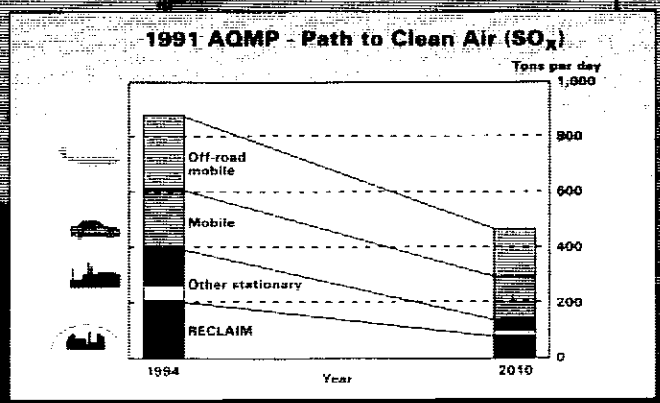


Figure 1. RECLAIM plays a significant role in Air Quality Management Plan inventories.

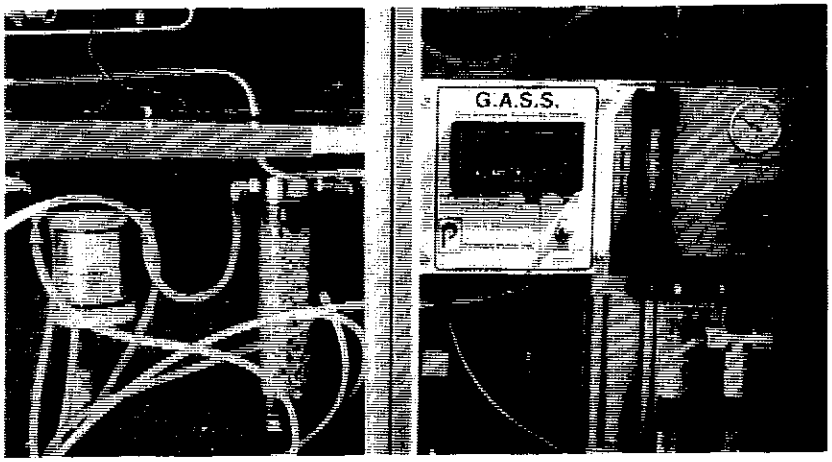


Figure 4. Permeation dryer at sample point (left) and phosphoric acid scrubber (right)

on the sample system plate after the sample cooler that was plugging regularly.

RATA tough to pass with low SO_2 levels

One source had extremely low SO_2 emissions, often in single-digit ppm levels. Measurements were made with an etalon-based SO_2 analyzer. Attempts to pass the RATA had been unsuccessful. The analyzer was slowly driven upscale when the calibration gas was injected directly through the probe and sample line while the RATA result showed almost zero. SO_2 was being lost somewhere in the sample system.

The first loss source explored was the sample lines. Some low points in the sample system could be collecting water, so nitrogen was flowed through the lines to dry them out. Although calibration response time improved briefly, RATA did not improve. The sample lines were set to run at 180°F, as had been done previously for NO_x systems. To eliminate water condensation, the lines were replaced with higher-temperature-capability lines. Although this was conceptually correct, it still did not help with the RATA.

After hearing about a competitor recently passing this same test, a Perma Pure permeation dryer, shown in Figure 4, was installed just after the probe box. This dries the sample at the sample point, reducing SO_2 condensation in the sample system. Once installed, the sample system dew point dried down slowly at first, proving there was more water in the system than originally thought. After a few hours, the moisture level bottomed out. Calibration gas response was very quick (less than a minute), and the RATA was passed using a spiking method. Since then, a similar system was also installed on the catalytic cracker unit.

Cylinder gas audits proposed and approved

The SCAQMD requires measurement of total sulfur in fuel gas instead of hydrogen sulfide. Although 10 sulfur species are defined, response factors are assigned based on methyl mercaptan. RECLAIM requires the reference test method for the RATA, which is based on a sulfur chemiluminescence detector, to be used. It also requires the samples to be collected in a bag and sent out for testing. At first, the SCAQMD was the only approved testing laboratory; however, Core Laboratories has also been approved.

Three refinery fuel gas systems typically have low total sulfur levels (i.e., less than 50 ppm). Attempts to pass the RATA were unsuccessful because the analyzers read higher than the reference method. After repeated attempts, the need for an alternative became clear. A cylinder gas audit (CGA) was proposed, as defined in 40 CFR 60, Performance Specification 2, Section 10. A CGA allows a known concentration gas to be used to test the analyzer system. It is applicable for many situations, especially when process emissions are much lower than the allowable level.

Since specific language allowing CGA was not included in the SCAQMD rules, refinery environmental and analyzer specialists proposed the CGA as an alternative. After negotiating measurement details, permission was granted to do the CGA. The relative accuracy requirement was reduced from 20% to 15% per the federal regulations. Cylinder gases for this audit could not conform to the EPA requirements for Protocol 1 gas as no standard reference materials (SRMs) exist for these levels of sulfur compounds. They were made to the supplier's best capability. For one analyzer's low-level check gases, only one compound, carbonyl sulfide, could be used because manufacturers would not guarantee the stability of any other reduced sulfur species.

The analyzers passed the CGAs as required. Based on outside testing resources available, the refinery would prefer to exercise this option as much as possible for sulfur species. However, until the National Institute of Standards and Testing (NIST) can provide gases at these levels, certified gases will have to be used.

Ammonium sulfates plug system

In a fluid catalytic cracking (FCC) unit, ammonia is often injected into the flue gas upstream of the electrostatic precipitator to improve SO_2 removal efficiency. Trace amounts of ammonia in the flue gas combine with SO_2 to form ammonium sulfates, which are blue to whitish crystalline substances. These salts are deposited in the sample system, slowing response and eventually plugging it off. Keeping the sample as hot as the process is one solution; however, the process temperature is over 500°F, making it impractical. Instead, the ammonia is neutralized

For further reading

South Coast Air Quality Management District (SCAQMD). July 1993. *RECLAIM: The Regional Clean Air Incentives Market,* Volumes 1-5.

South Coast Air Quality Management District (SCAQMD). *Annual Report.* SCAQMD World Wide Web page, http://www.aqmd.gov/monthly/annual95.html.

RECLAIM: Los Angeles's New Market-Based Smog Cleanup Program. March 1996. *Journal of the Air and Waste Management Association,* p. 203.

Behind the byline

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experience meant that Chevron had to provide almost all the rule interpretation knowledge. Chevron also had to define the hardware that would meet the regulatory definitions. It is not reasonable to expect engineering contracting firms to have this knowledge; there are not enough opportunities for them to do these kinds of projects, and staff turnover makes retaining knowledge very difficult.

Once again, engaging an environmental testing firm with a strong engineering background to provide technical guidance and work with your own capable staff appears to be the best solution. Such firms have the knowledge and experience to help guide your project. Their support could include:

- Evaluating your process to identify the best monitoring locations
- Identifying potential measurement interferents and selecting the best analytical technology to deal with them
- Developing a sample system that minimizes sample loss and degradation
- Performing required tests after all systems have been checked and verified
- Processing necessary, timely reports

The environmental testing firm should be involved as early as possible so it can influence early decisions in the process. Its concurrence will be a vital component of the project's success.

Allow time to work the project

It seems obvious, but the manpower to complete the work must be provided. Especially on a job this size, the technical and maintenance support required should be reviewed frequently to ensure that help will be there when needed. Although all projects have due dates and project schedules that must be adhered to, environmental projects have legally mandated deadlines. In addition to lost profits, fines may be levied if the work is not completed on time.

Depending on project scope, it may be best to put key technical and maintenance staff on special assignment to support the project. This will allow them to focus on the project rather than be torn between different priorities. If the work is completed early, there is no loss since the people can be returned to their original assignments.

Monitor certification contractor

In a meeting, the SCAQMD said it was essential that Chevron and others know whether the certification contractor was doing a good job. Although this may seem obvious, the project scope seems to preclude this. Chevron did not have anyone trained in these methods to follow them around. Nor was it felt that the contractor was doing a poor job. But in some situations, the certification contractor may not be as experienced or have adequate training. Currently, there is no qualification program for contractors; any qualifications are purely voluntary.

However, it is imperative that knowledge be developed in-house or an outside contractor be hired to audit the work done by the certification contractor. There are good training programs available from environmental contracting firms to develop basic knowledge. Training usually focuses on federal requirements; a special request may be needed for specific state or local information. Except in specific areas of the country, such as the area covered by the SCAQMD, you can do your own testing.

Another option is to hire a consultant to audit the work, although it may not be cost-effective for small projects. These consultants can be looked up in the Air and Waste Management Association (AWMA) annual directory of services. Be sure that the one chosen has local experience and do not forget verifiable references.

Work with permitting agency to develop rules

The engineer responsible for analyzer installation is typically not involved with rule development or modifications. This responsibility is usually left to the facility environmental specialist, whose experience in monitoring requirements may be limited. Fortunately, with RECLAIM, Chevron reviewed the rule during the proposal phase and developed a list of monitoring and technology issues. In a meeting with the SCAQMD technical staff, these issues were discussed and, based on these discussions, some monitoring requirements were changed in the final rule.

At a minimum, your environmental specialist should be aware of the schedule needs for a typical facility project. Frequently, environmental agencies will request six months. This might work if the facility has a project team already in place, scope developed, and front-end engineering complete on the day the rule is passed. One year is more realistic because the system must be commissioned before the RATA is attempted. A confusing rule will make that schedule extend even further.

Not all environmental monitoring projects are as complex as a RECLAIM project. Many lessons learned can be applied to environmental projects of any size. Get to know your environmental specialist and develop a relationship so you know when the next rule is being developed. IT