

# Developing a Catalyst Regeneration Procedure

Case history of how one ammonia plant operator gained useful experience and helpful knowledge in the regeneration of a chromium-based catalyst.

R. S. Collard,  
J. R. Simplot Co.,  
Pocatello, Idaho

A chromium-based, low-temperature shift (LTS) catalyst in the Pocatello, Idaho, ammonia plant of J. R. Simplot Co. can now be regenerated with the unit out of service only about 60 hr. That is for sulfur poisoning and ageing. If chlorine is involved, the time will be about 120 hr.

This article will describe the Simplot experience over recent years in the development of this satisfactory regeneration procedure.

Figure 1 is a simplified flow diagram of a 150-ton/day Chemico-designed natural gas reforming section built and started in 1964. The hot zinc vessel, natural gas heaters, and duplicate 150-ton/day plant were tied in at the April, 1974, shutdown. The original unit had been operated for almost ten years using activated carbon vessels for sulfur removal.

Table 1. Compositions of streams shown in Figure 1

Component	Stream No.			
	1	2	3	4
CH <sub>4</sub>	92.5	—	—	—
C <sub>2</sub>	5.8	—	—	—
C <sub>3</sub>	0.6	—	—	—
C <sub>4</sub> <sup>+</sup>	0.02	—	—	—
H <sub>2</sub>	—	67.5	60.4	61.5
N <sub>2</sub>	0.8	0.2	21.0	20.0
CO	—	7.1	2.0	0.15
CO <sub>2</sub>	0.2	15.0	16.1	16.9
Ar	—	—	0.2	0.2
S/G	—	1.2	1.0	1.2

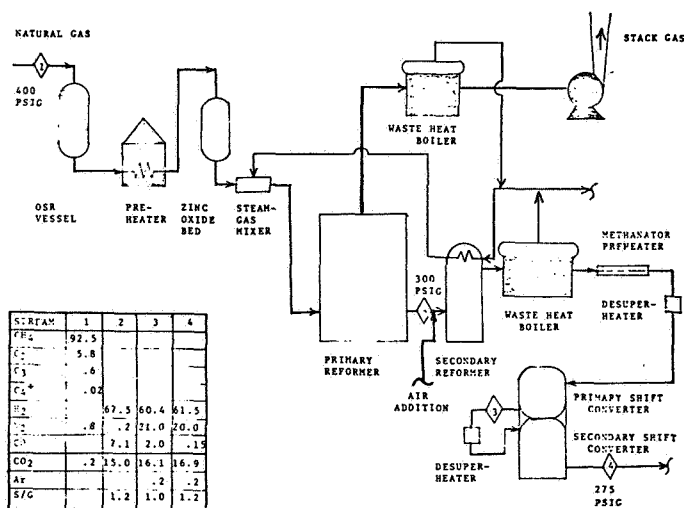


Figure 1. The 150-ton/day ammonia plant, Chemico design, at Pocatello.

## Chromium-based catalyst in use April, 1969

The plant is designed with stacked shift converters. The first shift is the top portion. The bottom portion contains the low-temperature shift (LTS) catalyst. A chromium-based catalyst, LSK from Haldor Topsoe, has been used in the low-temperature shift since April, 1969.

Temperature is controlled on each catalyst bed by use of a process condensate quench. The water comes from

the gas cooling area in the MEA system. The emergency system for water is a crossover from the discharge of the boiler feed water pump to the discharge of the desuperheater pump. Betz Hydrazine is used for O<sub>2</sub> scavenging, as sulfite would poison the LTS catalyst when emergency water was required.

The steam-to-gas ratio normally is maintained at 1.2:1 at the outlet of the low-temperature shift bed. The normal inlet CO is 1.8-2.0%. The pressure is approximately 290 lb./sq. in. gauge, and the dry gas flow to the low temperature shift is close to 700,000 std. cu. ft./hr., corresponding to a space velocity of about 2,000 std. cu. ft./hr. of dry gas per cu. ft. of catalyst because the LTS volume is about 340 cu. ft.

At the above conditions initially CO leakage is a little less than 0.1 mole % dry at catalyst inlet temperature of 400-410°F, which corresponds to chemical equilibrium composition. When leakage increases above the range 0.2-0.3 mole % dry, we prepare for replacement or regeneration.

The low-temperature shift catalyst is reduced with natural gas as a carrier and up-flow, to prevent over-heating the top of the catalyst by radiation from the diaphragm between beds. The LTS is bypassed every time process gas is stopped in the primary reformer. It is then purged with N<sub>2</sub>, depressurized to 25 lb./sq. in. gauge and we try to hold as much heat as possible. The catalyst is then heated with dry natural gas to 400°F before being returned in service. This is a carryover practice from our original catalyst supplier.

As indicated earlier, LSK was used in the second shift

since April, 1969. Another catalyst was used just previous to this charge and had about 30 months of satisfactory service life. But that catalyst type was not available in 1969, so it was decided to change suppliers, and the Haldor Topsoe Company was selected. We were pleased with the performance of LSK because CO leakage did not exceed 0.15 mole % (dry) until after about 30 months of operation. Another 340 cu. ft. was purchased as replacement in 1972.

During the past three years many different problems have occurred in the plant, yet we were again able to obtain three years of life with LSK. However, this resulted because it was possible to regenerate this catalyst. The money saved corresponds to a purchase of minimum two charges.

It should be explained, for the sake of completeness, that the charge operating now is actually not the second but the third charge of LSK. The second charge was only in the converter for about two months, April through May 1972, because it was over-heated during reduction.

There is no problem reducing LTS catalyst with natural gas as carrier as long as the temperature is kept below 400°F, no rapid temperature changes take place, and blinds are installed at all places where hydrogen containing gas or anything else can leak into the carrier gas flow.

Unfortunately, during that particular reduction of the second LSK charge, blinds had not been installed, and we are confident that the reasons for a sudden increase in converter inlet temperature from 200 to over 400°F were these. Water had leaked into the boiler feed water preheater which is used for heating natural gas; and after this water evaporated, temperature at bed inlet suddenly rose. Then later, bottom bed temperature went out of control, thereby damaging the batch before the reduction actually started.

### Three regenerations in three years

The present catalyst charge has been operating three years and has been regenerated three times. After each regeneration, operating conditions were restored as for new catalyst, i.e. CO-leakage of slightly below 0.1 mole % dry and catalyst inlet temperature of 400-410°F. Unfortunately, we have not been able to maintain these conditions as long as we would like, but taking the problems into account, we have been satisfied.

The first regeneration was carried out in September, 1973, after about 15 months operation and after problems with severe sulfur poisoning in late August. The plant is located between gas injection points on the interstate gas transmission line, and it started to receive Canadian gas down the line from Seattle, Wash. This gas contains some COS and has a higher H<sub>2</sub>S content. There was faster deterioration of LTS catalyst activity. A change in OSR regeneration procedure in an attempt to reduce losses did not succeed.

Late in August, 1973, some leakages were as high as 0.6 mole % at about 85% rate. The Topsoe representative in Houston, Tex., was called to discuss the catalyst decline and get some catalyst shipped to the plant. At that time, none was available. We didn't want to purchase another brand but couldn't operate the plant with the high

leakage for 30 to 40 days until new catalyst could be shipped.

Regeneration was recommended by Topsoe. We were apprehensive but after discussions decided to try it, and on September 17, 1973, regeneration was started. By September 21, the regeneration and reduction were completed and the unit returned to service. The methanator  $\Delta T$  leveled out at 10°F at 106% of design.

The second regeneration was done 14 months later in November, 1974, and carried out in connection with an emergency shutdown. There had many shutdowns in the previous year. Some problems were with the old plant and some the usual problems with the new plant being tied-in and started up.

During one particular shutdown, shortly before the regeneration, the reactor was filled with boiler feed-water during the heat-up cycle on the second shift due to an operator error in valve positions. The vessel with hot catalyst was thereby completely filled with hot water. After the incident, the leakage was almost twice what it had been previously.

### Regenerating for chlorine

The third regeneration took place in April, 1975. And as it comprised regeneration for chlorine, I will use this to describe our procedure. To regenerate for chlorine, the catalyst must first be oxidized whereby it is also regenerated to eliminate possible ageing and/or sulfur poisoning.

The regeneration was made when the plant was down about a week for some other repairs. But deterioration had actually taken place some three months earlier, namely late December, 1974, and early January, 1975. That was when desuperheater quench-water pump problems occurred and operation was on the emergency boiler feed-water crossover.

This allowed demineralized water to be used for quench. The demineralizers failed and some bad water was used for quench and boiler feed water. For about 10 days, some raw water was added. A 25-lb./sq. in.  $\Delta P$  developed across the the LTS bed. The raw water contains 30 ppm. chlorides.

After the water problem was resolved, the CO leakage leveled out and remained at 0.25 mole % dry. During an emergency shutdown, about January 10 (we were having many), a sample of catalyst was taken halfway up the LTS bed and sent to Copenhagen for analysis. It contained 300 ppm. chloride. This was, according to Haldor Topsoe, a surprisingly high figure to find halfway down the bed because a sample from the upper-most layer of the bed collected only two months before had contained only 400 ppm. of chloride.

The sample showed a chloride poisoning problem and it was decided to regenerate for chloride. The following describes the regeneration.

The first part of the regeneration consists of oxidation of the catalyst by air in a carrier flow of steam. Normal flow direction and normal operating temperature is used, thus it takes very little time to prepare for the oxidation. Purging of process gas is with steam which is vented downstream of the reactor; and the air is added at a suitable point upstream.

Steam flow is about 8000 lb./hr. and starts at about

400°F. Air is added until the temperature increase across the bed is about 100°F. When, after about 10 hr., there is no temperature rise across the bed, air flow is increased and temperature increased to about 650°F. These conditions are held about five hours, whereupon the system is coded.

If no chloride regeneration were involved, cooling would go to 300-350°F, blinds installed and reduction started with hydrogen in natural gas. For this particular regeneration where chloride regeneration was involved cooling was continued to about 325°F in steam, then switched over to cooling in natural gas. Cooling took about three hours at a flow rate of 25,000 std. cu. ft./hr.

The reactor was opened. It looked awful in the top—all white. There was a 2-in. layer of white dust, and below that about a 2-in. layer of catalyst which was glued together with the white material. The white material was found to consist mainly of silica and some calcium carbonate. The catalyst glued together contained about 1% of chloride. The catalyst just below the crust was free-flowing and the top of this catalyst contained about 700 ppm. of chloride.

The white material and crust were removed. Then we started washing the catalyst in up-flow with demineralized water. Washing was for 12 hr. at 20 gal./min. Washing water was not analyzed; it was black with catalyst dust.

After the reactor had been drained, the catalyst was black; it looked as if there was mud in it. The catalyst particles were strong but some catalyst dust adhered to the surface. A one-ft. layer of catalyst (35 cu. ft. approx.) was removed, but the catalyst still looked the same.

Catalyst drying was then started, with natural gas in a counter flow. Temperature of the natural gas was about 250°F, and pressure in the vessel between 30 and 50 lb./sq. in. gauge. Inasmuch as pores of the catalyst were completely filled with water, it took rather a long time to dry out at this temperature. Natural gas flow was first about 50,000 and later increased to 80,000 std. cu. ft./hr.; drying took about 30 hr. The next time superheated

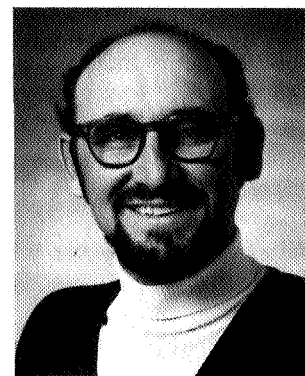
steam may be used for drying and at a somewhat higher temperature which the supplier said is possible.

### Decision to screen the catalyst

During the drying, pressure drop measurements indicated the continuing possibility of flow restriction further down in the catalyst bed. It was therefore decided to cool the catalyst, take it all out via the bottom manhole, and screen it. This operation took two more shifts.

The catalyst came out the bottom manhole onto a rotating screen. It was all free-flowing. There was no broken catalyst and no part of the catalyst which was weak nor any part which had agglomerated. The screening loss was very small, like that of new catalyst. All samples showed catalyst having high strength; and chemical analyses showed that chlorine had been completely removed.

All the catalyst except the 35 cu. ft. of wet catalyst which had been taken out just after the washing was immediately reloaded. The reduction went ahead the normal way, i.e. heating in natural gas and reduction with hydrogen in the natural gas at temperatures between 300 and 400°F. The flow during reduction is about 75,000 cu. ft./hr. which means that the space velocity is a little over 200 std. cu. ft./hr. gas/cu. ft. catalyst during reduction. #



R.S. Collard