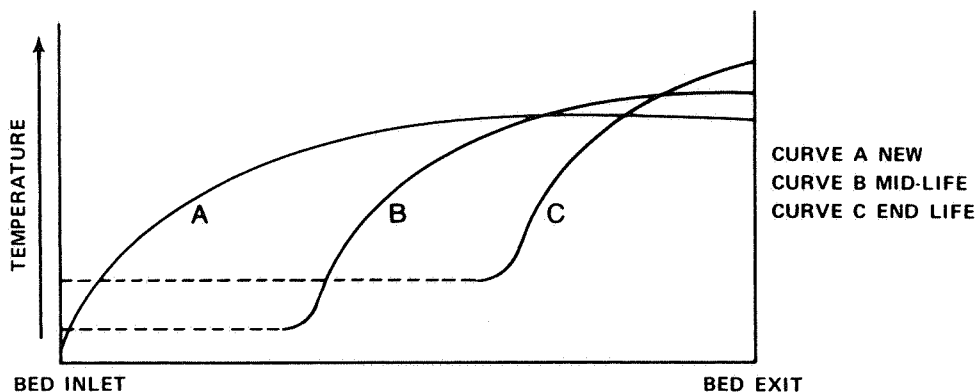


**Figure 1.**  
Temperature profile  
through  
catalyst bed.



Catalysts in Industry—

## Why Shift Catalysts De-activate

The development of guard catalysts which can rapidly react with chlorine for extended periods of time allows LT shift converters to be operated successfully when larger than normal levels of chlorine are present.

P. W. Young, Imperial Chemical Industries, Ltd., Billingham, Teesside, England  
C. B. Clark, Katalco Corp., Chicago, Ill.

The proportion of CO in the exit gas leaving an LT (low temperature) shift converter normally has a low value when the catalyst is new, and rises during the life of the catalyst. The useful life of the catalyst is the time which elapses before the CO reaches some limiting value. The factors determining the definition of this useful life of the catalyst are discussed in this article, as are some alternative ways of distributing LT shift catalysts to improve shift efficiency. In particular, the effect of chlorine on the catalyst structure is considered. The object of this article, however, is to suggest ways in which the performance of a converter can be extended in time. This ranges from selection of a stable catalyst to techniques for minimizing the effects of poisons, particularly chlorine.

When an LT shift catalyst charge is new, the reaction starts at the bed inlet and the temperature profile through the bed of catalyst has the form shown by curve A in Figure 1. With a new catalyst, the maximum rate of temperature rise should be at the bed inlet and the rate of rise at the exit should be very slow because the gas composition is close to equilibrium.

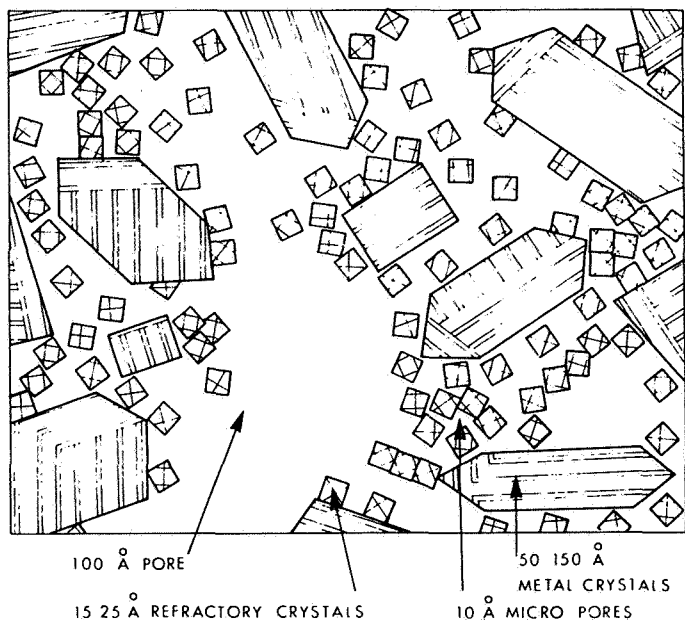
Curve B shows a typical temperature profile near the middle of the life of the catalyst. There is no temperature rise at the bed inlet and when reaction first starts it is slow. The later part of the curve is similar to curve A, but although the rate of reaction at the bed exit is higher

than in curve A, the overall temperature rise is slightly less than that obtained on new catalyst.

Curve C shows a typical temperature profile at the end of the life of the catalyst. It has been necessary to raise the inlet temperature to obtain the best possible performance and there is no reaction in a large section of the bed. When reaction starts it is still rapid, but the exit gas is further from equilibrium than in curves A and B. The exit CO from curve C is much higher than from curves A and B.

Some reactors have a moving thermocouple, making it possible to measure curves similar to those in Figure 1. Reactors in which only a few intermediate temperatures can be measured will usually show a similar behavior. This, the typical pattern for die-off of an LT shift catalyst operated under favorable conditions, is also a clear indication that a poison is entering the converter and deactivating the catalyst.

It is largely because poisons enter the converter that it becomes necessary to change the catalyst. Consequently, a knowledge of what these poisons are and what they do to the catalyst is of considerable interest. First, it is necessary to discuss what kind of structure a low temperature shift catalyst has, and then to examine the initial evidence, mainly from the laboratory, of how poisons affect the structure. Of principle interest to LT shift users, however, is the



**Figure 2. Hypothetical picture of a metal plus refractory catalyst prepared by precipitation and reduction.**

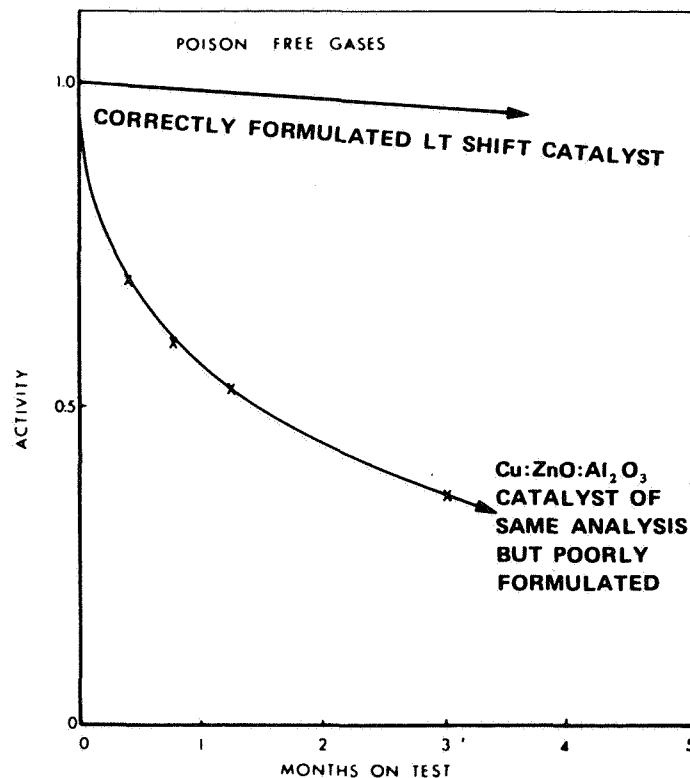
application of the laboratory findings to the operation of a full-scale plant, a matter to be discussed later.

### Low temperature shift catalyst

Probably all commercially available LT shift catalysts are based on metallic copper, and copper appears to be the only active catalyst component. A catalyst containing 100% copper, in a sufficiently finely divided form, should therefore be the most active material for this duty. At LT shift operating temperatures, however, small crystals grow by a sintering process and it can be calculated that the minimum size of copper crystals, after six months operation at these temperatures, would be about 10,000 Å dia. As a consequence, the available surface of copper would be small and the LT shift reactor would have to be several times larger than current vessels. Because crystal growth is a general phenomenon in catalysts containing finely divided active crystals, there is little value in discussing the initial activity of catalysts and it is more meaningful to compare stable activity of LT shift catalysts after, say, six months of operation.

In order to make a useful LT shift catalyst, the copper crystals must be both small and stable. The addition of a second component into the formulation, such as zinc oxide, assists in the process of stabilization of copper crystals by acting as a spacer material. The size of the stable copper crystals depends on the stability of the spacer material at the operating temperature, so it is this property of the zinc oxide component which principally defines the behavior of the LT shift catalyst in service. The size of copper crystals stabilized with zinc oxide alone is in the range 100- to 200 Å.

Some catalysts contain copper, zinc and alumina compounds so that, in the final catalyst, copper is stabilized by both zinc oxide and alumina. The alumina can be manufactured as very small crystals and, because alumina has a high melting point, the stable crystals formed have diameters around 40 Å. The resultant catalyst can be shown to contain copper crystals, after about six months of operation, of around 80 Å dia.



**Figure 3. Thermal stability of catalyst formulation.**

Figure 2 is a diagram of a good LT shift catalyst.

The stable activity of catalysts of this type should, therefore, be roughly 50% higher than the stable activity of other LT shift catalysts. This has been measured under poison-free laboratory conditions, Figure 3. Of more interest to catalyst users, however, is the fact that this effect has also been demonstrated on several plants when normal poisons were present, as illustrated in Figure 4A. This graph shows the temperature profile through a bed of catalyst in operation in the U.S. at different stages in the life of the catalyst. To simplify comparison, the same inlet temperature has been used for the measurements throughout the life. The slope of the curve at the middle and end of life is the same as that of new catalyst. In Figure 4B we have calculated the temperature profile expected from a catalyst with a stable activity two-thirds that in Figure 4A. The slope for aged catalyst is less steep, and so the overall temperature rise (which measures the conversion of CO) is lower than in Figure 4A.

### Chlorine as a catalyst poison

The quantity of chlorine present on most industrial plants is below the level which can be detected by convenient analytical techniques so its effects have only recently been investigated in detail.

Since the quantity of sulfur found in discharged catalysts is frequently 10 times higher than the quantity of chlorine, it was natural to assume that sulfur was a more serious hazard than chlorine. Typical quantities of chlorine, found on LT shift catalysts after two years of operation, are 0.05 wt. %  $\text{Cl}_2$  at the inlet and less than 0.02 % at the exit. As the chlorine found on the catalyst at the top of the bed is always considerably greater than that found at the exit, it is fair to assume that nearly all the chlorine entering the converter reacts with the catalyst. Hence, the typical average quantity of chlorine

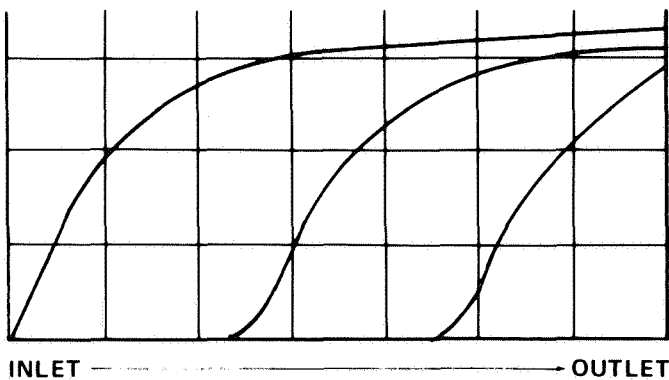


FIGURE 4-A - LT SHIFT CATALYST OF ACTIVITY A

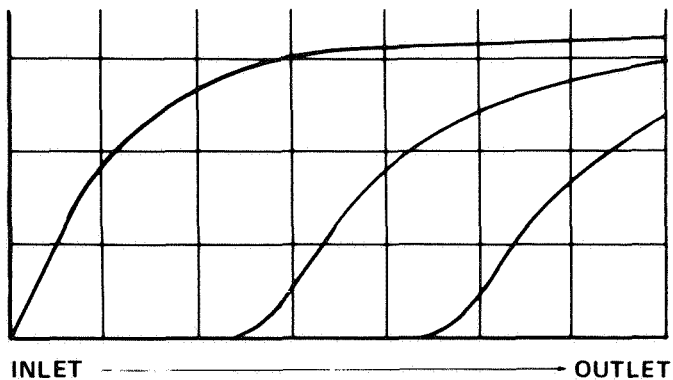


FIGURE 4-B - LT SHIFT CATALYST OF ACTIVITY  $\frac{2}{3}$  A

Figure 4. Effect of stable activity on exit CO.

in the process gas and steam is 1 g. of chlorine in every 60 million std. cu. ft. of wet process gas. We are, therefore, compelled to ask the question, Can this very small quantity of chlorine affect the performance of the catalyst?

Under laboratory conditions, even when sulfur is removed, LT shift catalysts show rapid loss in activity unless precautions are taken to remove chlorine. Laboratory work on sulfur poisoning shows that LT shift catalyst is poisoned by sulfur when  $H_2S$  is added, but the activity is completely restored shortly after the addition of the  $H_2S$  stops. Formation of cuprous sulfide, at  $450^\circ F$ , requires an  $H_2S$  concentration around 3 parts/million, which is much higher than is found in a commercial plant, so the poisoning by sulfur is probably due to a surface effect and not to the formation of a compound with copper. Zinc sulfide can form with an  $H_2S$  concentration of  $5 \times 10^{-3}$  parts/million  $H_2S$ , so chemisorbed sulfur on the copper surface can be expected to react with zinc oxide. This explains why the poisoning is only temporary. In consequence, the loss of activity of LT shift catalysts on full scale plants cannot be ex-

plained entirely by reference to sulfur and it is necessary to consider the effects of chlorine.

When chlorine reaches an LT shift catalyst it causes an immediate loss in activity, and even after the source of chlorine has been removed the catalyst continues to lose activity. The rate of loss in activity decreases as the time after the chlorine addition increases. In a commercial plant it takes about four to six weeks for the catalyst to stabilize after it has been poisoned by chlorine. In consequence, the final effect of the poison is considerably greater than the initial effect, Figure 5. Zinc chloride is found in the catalyst after chlorine has been added.

Zinc chloride melts at LT shift operating temperatures so it is not surprising that traces of zinc chloride in the zinc oxide particles cause the zinc oxide crystals to grow. We have already shown that the size of the zinc oxide spacer crystals was the factor which determined the stable size of the copper crystals. Growth of the zinc oxide crystals, induced by chlorine, causes growth in the copper crystals and the catalyst loses activity.

In short, small quantities of chlorine added to the catalyst cause a large drop in catalyst activity even in catalysts where the presence of small crystals of  $Al_2O_3$  assists in stabilizing the zinc oxide crystals. Consequently, the behavior of commercial charges of LT shift catalysts, in terms of performance and lifetime, is

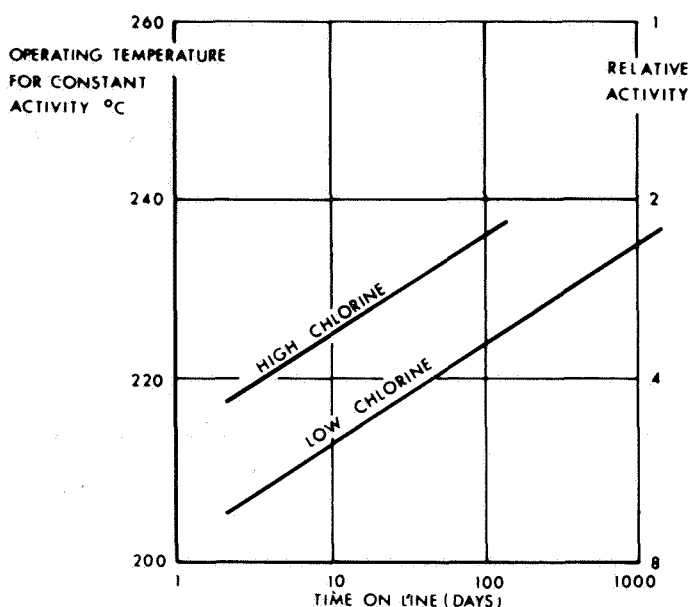


Figure 5. Loss of activity due to metal crystal growth in a supported copper catalyst.

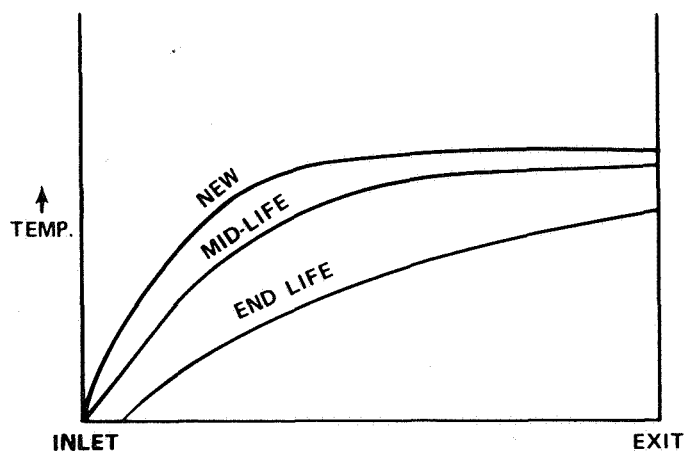


Figure 6. Temperature profile through LT shift catalyst subjected to condensing steam conditions.

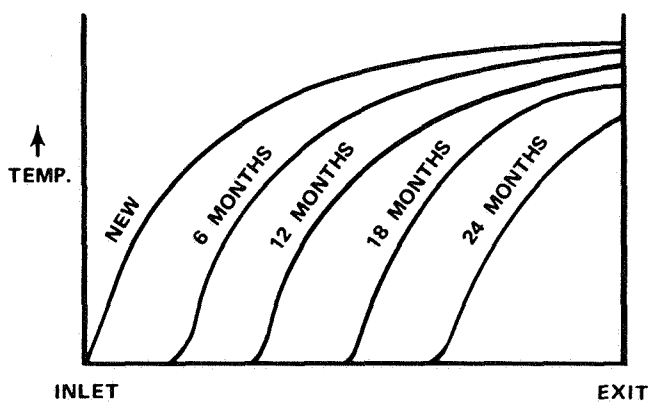


FIGURE 7-A  
CATALYST OF STABLE ACTIVITY A

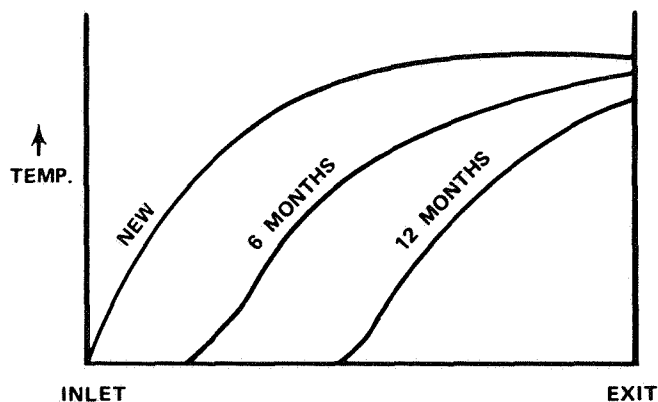


FIGURE 7-B  
CATALYST OF STABLE ACTIVITY  $\frac{2}{3}$  A

Figure 7. Temperature profiles at different times during catalyst lives.

largely determined by the way in which chlorine is distributed through the bed of catalyst.

In the laboratory, at atmospheric pressure and using freshly reduced LT shift catalysts, experiments with radioactive tracers show that 90% chlorine removal is achieved at a space velocity of 10,000 hr.<sup>-1</sup>. With extruded zinc oxide impregnated with copper, the observed rate of reaction was approximately 1/20 of the rate observed on fresh LT shift catalyst. Rate of reaction appears, therefore, to be related to the surface area of the catalytic surface.

In a commercial plant, pressures higher than atmospheric are normal so the rate of reaction of chlorine with freshly reduced catalyst should be higher than the rate measured in the laboratory. Consequently, concentrations of chlorine should fall rapidly along the bed, and effects due to chlorine should only be expected at the inlet to the bed. This is indeed the case with a new charge of catalyst where the effects of chlorine are confined to the first 10%, or less, of the bed.

Since one of the effects of chlorine on LT shift catalysts is to cause a progressive loss in surface area, there will be a loss of area in the catalyst at the inlet. Consequently, the chlorine reaction will become slower and chlorine will penetrate further into the bed. After a time, the catalyst loses almost all of its activity because the CO shift reaction and its effectiveness for chlorine removal also falls. Subsequently, the rate of chlorine removal falls to a low value at the bed inlet, but rises further along the bed when the chlorine containing gas meets more active catalyst, and finally falls after most of the chlorine has been removed.

Chlorine removal is, therefore, accomplished in a band of catalyst which is at the inlet when the catalyst is new and which moves progressively down the bed as the catalyst becomes older. This is the pattern of behavior shown in Figures 1 and 4. Clearly the end of life of the charge is the time at which the proportion of unpoisoned catalyst is just sufficient to achieve the required CO conversion duty.

Anything which will decrease the rate at which chlorine can penetrate the bed of catalyst will increase the life of the catalyst charge. This is why operation in a good clean plant will give better lifetimes than elsewhere. It follows that a catalyst with a high stable activity should rapidly absorb chlorine with a relatively slow loss in activity. This is probably the reason why quality of the LT shift catalyst is still important in achieving good lifetimes when chlorine is present.

### Catalyst operation in commercial plants

No plant can run under ideal conditions so catalysts must withstand the normal levels of chlorine which are present. Here we will discuss some adjustments to operating techniques which may extend catalyst lifetimes.

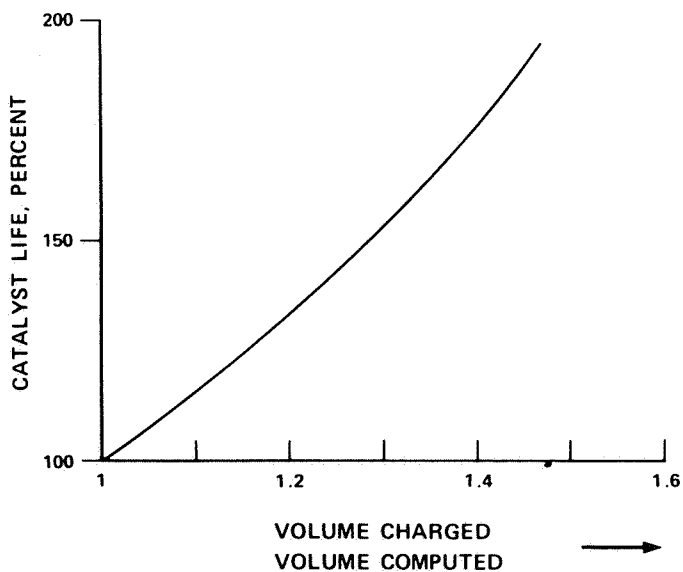
Any plant which experiences higher than average levels of chlorine will notice that lifetimes are short, a topic to be discussed later in this article.

Perhaps the most striking way in which performance and lifetime can deteriorate is to permit water to condense on the poisoned catalyst at the inlet and re-evaporate on an unpoisoned region of the bed. A marked fall in the activity of this region follows over the next four to six weeks. There are a few plants which are unable to avoid condensing water during startup. One such plant we know of experiences lifetimes of around 65% normal. The temperature profile along the bed on this plant shows the catalyst is losing activity along the whole bed, Figure 6.

A rise in the operating temperature has very little effect on the stable activity of an unpoisoned LT shift catalyst. In the region where chlorine is reacting with active catalyst, however, a rise in temperature will increase the rate at which zinc oxide crystals grow and will, consequently, increase the rate at which the catalyst loses activity. This is quite a marked effect on unstabilized LT shift catalysts, and their lifetime can be shortened by permanently raising the operating temperature. With a good, stable catalyst, temperatures up to 500°F can be employed without noticeably affecting the lifetime or performance; in the absence of poisons this could be 550°F.

Some plant designers, realizing that the exit CO can be very low when the steam ratio is high, use extra steam and cut down on the size of the LT shift converter. These plants increase the risk of short lifetimes and the following are probably all contributory causes:

1. The quantity of catalyst available for removing poisons is decreased.
2. A wider band of catalyst is needed to remove poisons when the wet gas flow rate is increased by the addition of steam.
3. Steam may contain significant quantities of chlorine.
4. The risk of condensation causing chlorine transfer is increased.



**Figure 8. Correlation between volume of catalyst and catalyst life.**

A low catalyst volume decreases the life of a charge, as does a catalyst with a low stable activity. A decrease in catalyst activity results in a wider band of catalyst being required for chlorine removal which, in turn, means that the rate at which the band moves through the bed is increased and the lifetime is shortened. In Figures 7A and 7B the life of two catalysts, one with two-thirds the activity of the other, are compared under conditions where the same concentration of chlorine is present in the inlet gas. (For convenience of presentation the inlet temperature has been held constant.) The time scale is typical of performance at wet gas space velocities of 5,000 hr.<sup>-1</sup> and shows that the less active catalyst requires 50% more catalyst to absorb the poison and also 50% more catalyst to perform the duty. In this example, the higher activity catalyst can be expected to last twice as long as the catalyst with the lower stable activity. At very low space velocities, when both catalysts would live much longer, the higher activity catalyst would have a 50% greater lifetime. At higher rates of poisoning, however, this catalyst could have a lifetime more than double that of the less active catalyst.

LT shift catalyst lifetime can be shortened by lack of adequate precautions during initial reduction. If the activity of the freshly reduced catalyst is below the maximum stable activity then maximum lifetime cannot be obtained. There is always pressure on plant operators to speed up catalyst reduction and initial performance remains good even when catalyst activity is below maximum. One of the reasons why modern LT shift catalysts have proved successful is that their stable nature makes reduction much safer and more reliable, and full activity, therefore, relatively easily achieved.

Reduction in steam causes some loss in activity and accordingly some decrease in lifetime. The activity loss is dependent on the speed at which reduction is done and also on the pressure used.

Chlorine appears to be present on all plants and for the majority of catalyst users the requirement is to increase the lifetime of the charge. Based on our experiences with well over 100 charges of LT shift catalyst in operation our recommendations can be summarized as follows:

1. Use a well-formulated, stable catalyst as described

**Table 1. Change-out costs.**

	Case 1	Case 2	Case 3
Catalyst Cost	120,000	120,000	120,000
Lost Production	125,000	37,500	25,000
Extra labor, Hydrogen & Gas Costs for loading & Reduction, etc.	5,000	5,000	5,000
Total	250,000	162,500	150,000

earlier in this article.

2. We have established a correlation of how increased volumes of catalyst increase catalyst life. This we describe as the catalyst's "self-guarding" property and is shown in Figure 8.

3. When chlorine concentrations are serious use a good chlorine-guard catalyst on top of or preceding the LT shift catalyst.

### Chlorine guard catalysts

The quantity of guard catalyst which can be installed in a converter is limited by the space available. Fresh LT shift is an excellent chlorine guard and *alternatives should be judged by comparison with it.*

The first type of material which was used as a guard catalyst was spent LT shift catalyst taken from the bottom of a converter. This requires reoxidation before it can conveniently be charged and must be re-reduced before use. The surface area, therefore, can be expected to be low and, in consequence, the rate of reaction with chlorine is slow. Porous forms of zinc oxide are very effective guards when new, but undergo a rapid loss in surface area. At wet gas space velocities below 1,000 hr.<sup>-1</sup> they can be used as an effective chlorine guard, but for this duty it would require the guard bed to be larger than the LT shift converter. Another common form of zinc oxide is impregnated with copper. Laboratory measurements suggest that this type of material is less effective than a good new LT shift catalyst.

The type of guard catalysts described above have a limited life because, in the presence of chlorine, surface area soon falls and the proportion of chlorine absorbed by the guard catalyst becomes too small to be of value. In the presence of significant quantities of chlorine they are unlikely to be effective for more than three to six months and similar protection can be obtained by installing one-third of the available volume with LT shift catalyst.

On plants where the level of chlorine is higher than average, the guard catalyst must absorb higher than average quantities of chlorine. One catalyst supplier has developed a modified LT shift catalyst in a manner which improves its capacity for chlorine absorption. Being an LT shift catalyst containing zinc oxide and alumina, this guard catalyst has high porosity with a high and relatively stable surface area. When new, it absorbs chlorine as rapidly as does normal catalyst and its LT shift properties are also valuable. A typical duty for this guard catalyst would be in a plant where the high level of chlorine would cut the life of a charge of LT shift catalyst from two years to one. The chloride guard catalyst would enable the hoped-for two year life to be restored or at least approached.

In the duty described above the guard catalyst is acting as an effective guard for about 12 months. Longer periods are possible when the concentration of chlorine is lower but, because chlorine absorption lowers the surface area of the guard catalyst, the catalyst is unlikely to be

**Table 2. Correlation between CO leakage and payback time.**

CO Leakage From LTS Reactor (% Dry Gas)	Assumed Lowest Possible CO Leakage	CO Differential	Pay-Back Time (months)		
			Case 1	Case 2	Case 3
0.35	0.25	0.1	24	14	12-13
0.45	0.25	0.2	12	7	6-7
0.5	0.25	0.25	9-10	5-6	5
0.6	0.25	0.35	7	4	3-4
0.7	0.25	0.45	5-6	3	3
1.0	0.25	0.75	3-4	2	1-½-2

an effective guard for more than 18 months. The life of the total charge of catalyst is, of course, much longer than the life of the guard.

When a very long life is required from the guard it is necessary to use materials which do not change when chlorine is absorbed. A catalyst of this type has been developed and absorbs chlorine without losing surface area and has proved useful for this type of severe duty. The catalyst is not an LT shift catalyst, which is its main disadvantage, but it is as effective as the modified LT shift catalyst previously described and has a longer useful lifetime.

### Decisions on catalyst change-out

The monetary value of reducing the carbon monoxide leakage from an LT shift reactor can be assessed for any plant, and this value can be used to optimize the use of low temperature shift catalyst and to decide the best time for catalyst replacement. A study was recently completed in a Kellogg 1,000 ton/day plant where additional conversion of 0.1% CO in the LT shift reactor had the following effect:

Feedstock Rate	Unchanged
Fuel Rate	Unchanged
Decrease in Methane in	
Make up gas	58,000 std. cu. ft./hr.
Decrease in Purge Rate	390,000 std. cu. ft./hr
Additional N <sub>2</sub> + 3H <sub>2</sub> in	
Make up gas	260,000 std. cu. ft./hr
Additional power required	
to maintain synthesis	
pressure	343 h.p.
Extra ammonia produced	4,730 ton/yr. (13 ton/day)
Value (at \$25.00/ton)=\$118,250.00/yr. (\$325.00/day)	

A full charge of low temperature shift catalyst costs roughly \$100,000 to \$140,000. This covers the range of costs from the major North American suppliers.

The cost of a catalyst change-out in terms of lost production, labor, gas, etc. has been estimated at \$125,000 (5 days, 1000 ton/day, \$25.00/ton). However, there are basically three situations to consider:

1. When the plant has to shut-down solely because of the LT shift.
2. When the plant has to shut down for other reasons and it is decided to change LT shift during the shutdown.
3. When the LT shift is changed with the plant operating at reduced rates and the LT shift bypassed.

In case #2, some of the cost of the shutdown may have to be carried by the LT shift if the shutdown is prolonged because of the LT shift change-out and reduction. Typically, 36 hr. lost production can be costed to the LT shift change-out estimate. In case #3 the lost ammonia production can usually be estimated at about 50% for the number of days at reduced rates, estimated at 2 days.

The total costs of the change-out for these three cases is summarized in Table 1.

Different companies have different rules for required pay-back times on capital expenditure in the plant. Where LT shift is involved, if the pay-back time is 12 months or less, a change-out of catalyst can usually be justified because the modern, stabilized LT shift catalysts will, with reasonable care and attention, give reliable and adequate performance for 1½ years with the exit gas CO level at, or close to, equilibrium at a 410- to 425°F inlet temperature.

Let us assume this CO level is 0.25%. (see Table 2.) In the type of plant being discussed, some variation in the CO level achieved occurs from plant to plant. This is due to slight differences in steam:dry gas ratio or in the heat exchange systems which control the minimum inlet temperature to the LT shift vessel. Thus, the figure in column 2 of Table 2 may be as low as 0.20, or as high as 0.32 and for this reason the figure in column 3, the "CO Differential" is the important figure.

### Conclusions

In commercial plants, the lives of LT shift catalysts are usually determined by the extent to which chlorine penetrates the catalyst bed. A catalyst with high stable activity can react rapidly with chlorine and it is this self-guarding property which appears to enable a well-formulated catalyst to have a long lifetime when chlorine is present.

The development of guard catalysts which can react rapidly with chlorine for extended periods of time allows LT shift converters to be operated successfully when larger than normal levels of chlorine are present. #

**P. W. Young** completed his B.Sc. at Leeds University in England. He has worked with ICI at Billingham since 1951. Starting as an analyst, then researching into high temperature chemistry, he moved into manufacture as a plant manager before returning to the Research Dept. in 1961 to study the production of copper catalysts and the reactions these catalyze. Since 1965 he has been in the Marketing Dept. where he pays special attention to CO conversion catalysts.



**G. Clark** received his B.S.Ch.E. degree from the University of Idaho. After graduation he joined Shell Chemical Co. first as a development engineer in San Francisco and later as a process engineer at the St. Helens, Oregon ammonia plant. He joined Katalco as a technical service engineer early in 1971 and has worked extensively on low temperature shift catalysts and service work for the ammonia and hydrogen plant industry.



## DISCUSSION

**JOHN S. CROMEANS**, Catalyst Consulting Services, Inc.: Concerning the reported poisoning of low temperature shift catalyst by chlorides, we have independent data confirming this is a very serious problem where chlorides are present in the feed. We recall a case where we were working with a hydrogen unit using feed gas from a platformer source. This

gas contained chlorides and we could not get these out of the system with the equipment available, so we proceeded to place a new charge of low temperature shift catalyst in service and it died in about 30 days. The chlorides just gradually killed it. We were operating with about 17 parts per million of chlorides in the feed at the time.