Meeting future SO_2 emission challenges with Topsøe's new VK-701 LEAP**5**™ sulphuric acid catalyst

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Kurt Christensen

Haldor Topsøe A/S
Nymøllevej 55, DK-2800 Kgs.Lyngby, Denmark

Introduction

Caesium-promoted vanadium catalysts, which have been available since the late 1980ies, have proved very efficient in reducing SO_2 emissions from sulphuric acid plants by providing high activity at low temperatures.

In 1996, Topsøe introduced VK69 designed for operation in the final passes of double-absorption plants [1, 2]. This catalyst offers a very significant activity advantage compared to potassium-promoted catalysts and earlier caesium-promoted catalysts. By installing the VK69 in the final pass of existing 3:1 double-absorption plants, the SO_2 emission can be cut in half, or the acid production rate can be boosted by 15-20% without increasing SO_2 emissions. SO_2 emissions below 100 ppm became possible in 3:1 double-absorption plants with the VK69.

However, still more stringent regulations have placed new demands on the sulphuric acid industry to lower SO_2 emissions and achieve conversions typically in the range of 99.8-99.95% (0.3-1.3 kg SO_2/MT H_2SO_4, 0.7-2.6 lbs/ST) for double-absorption plants and more than 98-99% (6.5-13 kg SO_2/MT H_2SO_4, 13-26 lbs/ST) for single-absorption plants. For many existing plants, the lower emission limits are a challenge at their current or future production rate.

Topsøe has responded to the new market demands by developing a novel catalyst, VK-701 LEAP**5**™, designed for operation at low temperatures in converted strong gases. By offering exceptionally high activity, this novel catalyst pushes the limits for industrially achievable SO_2 conversion in both single- and double-absorption plants.

Background

Commercial sulphuric acid catalysts are based on vanadium oxides promoted with alkali-metal sulphates on an inactive porous silica support. The catalysts are so-called supported liquid phase (SLP) catalysts, where the oxidation of SO_2 takes place as a homogeneous reaction in a liquid film covering the internal surface of the support material as illustrated in Figure 1.

The alkali promoters are mainly potassium and sodium but caesium is also used in some catalysts, because it provides excellent low-temperature activity. In spite of numerous investigations and publications on the coordination chemistry of the catalytic melt and the reaction mechanism, the details of the mechanism are still not entirely known. However, there is substantial evidence that only oxidation state V^{5+} is active in the catalytic cycle in the form of a dimeric vanadium oxosulphato complex [3].

At steady-state, the distribution of vanadium species in the catalytic melt are in equilibrium with the surrounding gas causing certain amounts of V^{5+}, V^{4+} and V^{3+}. However, V^{4+} and V^{3+} compounds do not contribute to the catalytic activity. The degree of reduction increases at low temperatures and high SO_2 partial pressure, and in addition some V^{4+} compound precipitates at temperatures below 460°C (860°F) and gradually depletes the melt of V^{5+} if the temperature is further lowered. This reduction and partial solidification eventually cause the activity to drop to practically zero at some minimum temperature of about 360°C (680°F) for a standard potassium-promoted vanadium catalyst.

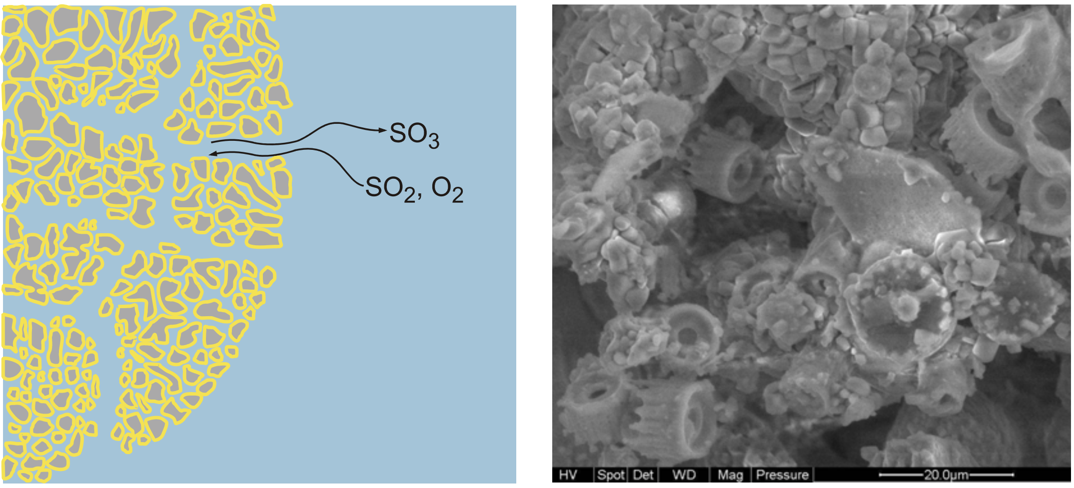

Figure 1. The active phase in a VK catalyst is a liquid film covering the internal surface of the silica support. To the right, a scanning electron micrograph shows the interior of a sulphuric acid catalyst at room temperature, where diatom skeletal fractions more or less covered with solidified catalytic melt are discernible.

The reaction rate for a catalyst may be limited by external mass and heat transfer to the pellet surface, by internal mass transfer in the porous support or by the intrinsic reaction rate itself. For sulphuric acid catalysts operating at a low temperature in high gas strength, the main limitation is the intrinsic reaction rate. The intrinsic reaction rate depends on the chemistry in the catalytic melt, but to a great extent, also on the distribution of the catalytic melt on the support and gas solubility and transport through the melt. At steady-state, the physical distribution of the melt is in equilibrium with the surrounding gas, and the distribution depends on the nano-scale surface properties of the silica support, e.g. the wettablility and surface tension. For existing commercial sulphuric acid catalysts, activity is seriously hampered by deep pools of catalytic melt restricting gas transport in the active phase.

Topsøe has now developed a completely new catalyst called VK-701 based on our novel LEAP**5**™ technology which overcomes these limitations and provides outstanding activity. The improvements, which include a very high V^{5+} content, have been accomplished by:

- Changing the intrinsic morphology and surface properties of the carrier.
- An optimised active phase for high SO_3 concentration.

The first ideas for the new catalyst were tested in lab-scale, and, based on confirmed high activity of the new formulation, development was continued with pilot-scale production and tests. Extensive testing again showed excellent activity and stability of the product with mechanical strength and pressure drop on target. We installed and optimised a new unique production line necessary for the manufacture of our new LEAP**5**™ technology catalyst. Full-scale production was carried out and all performance parameters of the VK-701 product were confirmed.

Properties and performance of VK-701 LEAP5™

The new VK-701 LEAP**5**™ is designed for operation at a low temperature in converted strong gases. A photo of the catalyst is shown in Figure 2 and the catalyst characteristics are summarised below:

Catalyst name:	VK-701 LEAP**5**™
Size and shape:	12 mm Daisy
Application :	Lower passes of single-absorption plants Third pass of 3:1 and 3:2 double-absorption plants
Operating temperature:	400-500°C (750-930°F)
Ignition temperature:	310°C (590°F)
Thermostability:	650°C (1200°F)

The choice of pellet size is a trade-off between activity and pressure drop. Pore diffusion limitations are modest in converted strong gases, and consequently VK-701 is produced in a standard size of 12 mm Daisy which provides lower pressure drop than the 9 mm Daisy. The pressure drop per bed height is equal to that of the well-known 12 mm Daisy products (VK38, VK48 and VK59).

Because the catalyst composition of VK-701 is based on well-known sulphuric acid catalyst materials, no additional efforts are required for disposal of the spent catalyst.

Figure 2. The new VK-701 LEAP**5**™ catalyst in 12 mm Daisy shape.

The activity of VK-701 operating at high conversion in a feed gas with 10% SO_2 and 10% O_2 is compared to the traditional Topsøe products, VK48 and VK59, as a function of temperature in Figure 3. Compared to standard potassium-promoted VK48, the VK59 provides significantly higher activity at temperatures below 430°C (805°F) due to its content of caesium. The new VK-701, however, exceeds the VK59 activity by about a factor two in the entire temperature range.

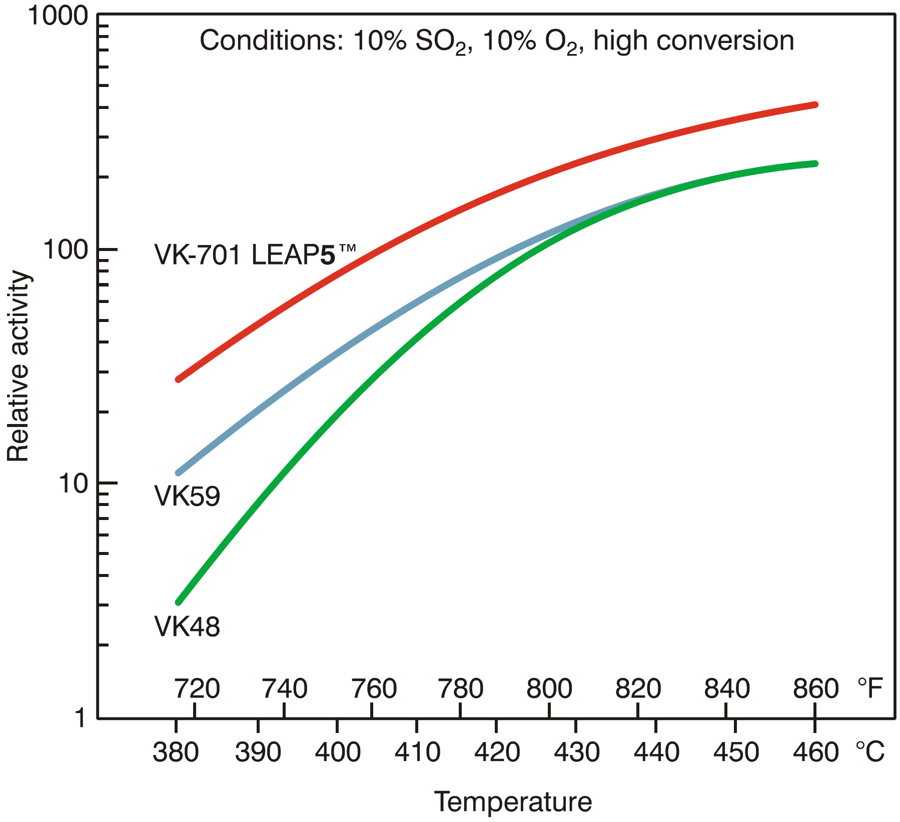

Figure 3. Activity of the new VK-701 catalyst in comparison with VK48 and VK59.

High levels of V^{5+}

A major leap forward for the LEAP**5**™ technology is the high amount of vanadium in oxidation state V^{5+} in the catalytic melt. The VK-701 is produced with fairly high vanadium content but not so much higher than for other commercial catalysts. Once in operation in the plant, however, the chemical composition of the active melt will adjust to the conditions of the surrounding gas. In order to study this equilibration in greater depth, we have measured the contents of different vanadium oxidation states in our laboratory. Catalyst samples were crushed and screened to a size fraction of 1-2 mm particles. The particles were loaded in an isothermal glass reactor and operated in 93% preconverted feed gas containing 10% SO_2 and 10% O_2. After one day of operation, the samples were quickly quenched to room temperature in nitrogen and subsequently analysed for their contents of V^{5+}, V^{4+} and V^{3+} by a three-step redox titration method.

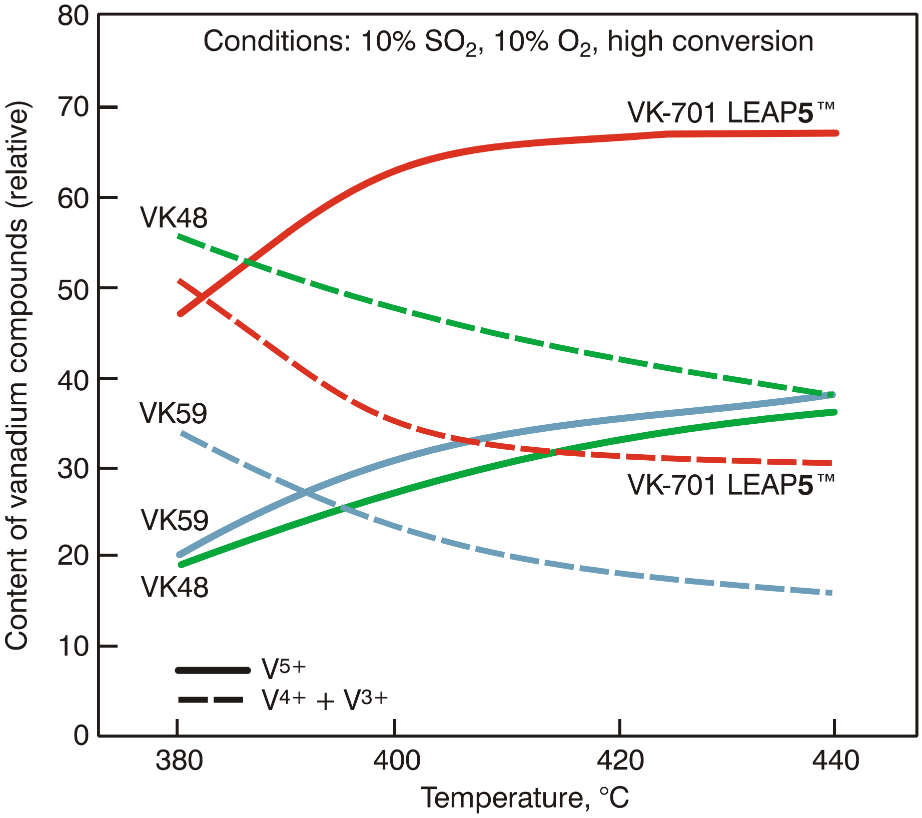

Figure 4. Content of different vanadium oxidation states in VK-701 (red curves), VK48 (green curves) and VK59 (blue curves).

Analysis results show that all three oxidation states are present under these conditions, although the V^{3+} content is very low. VK48 standard catalyst contains some active V^{5+} at 380-440°C, but most of the vanadium is actually in the inactive V^{4+} and V^{3+} forms as shown in Figure 4. The caesium-promoted VK59 catalyst contains less reduced vanadium but about the same amount of V^{5+} as the VK48. At 380-400°C the V^{5+} content is even lower for all three catalysts because V^{5+} is reduced to V^{3+} and V^{4+} by SO_2.

The situation is markedly different for the VK-701 LEAP**5**™. This catalyst contains much more active vanadium V^{5+} corresponding to about 70% of the total vanadium content at 400-440°C. The VK-701 contains two to three times more active vanadium than the commercial catalysts available on the market today.

Case studies

Two examples of VK-701 LEAP**5**™ applications are given in the following:

Example 1: Reduced emissions from a single-absorption plant

The SO_2 emissions from an existing single-absorption plant can be reduced significantly by loading VK-701 LEAP**5**™ as a replacement for conventional catalysts in the final pass.

Layout:	4-pass single-absorption plant with indirect cooling
SO_2 source:	Metallurgical off-gas
Feed gas:	8.5% SO_2, 14.7% O_2
Catalysts in beds 1/2/3:	VK38 / VK38 / VK48
Conversion outlet bed 3:	97.5%

Table 1 shows the performance of the new VK-701 catalyst in the fourth pass compared to standard potassium-promoted VK48 and caesium-promoted VK59. The total conversion of 98.57% achieved with VK48 can be increased to 98.74% corresponding to 12% lower SO_2 emission by replacing the VK48 with VK59 and lowering the temperature by 10°C.

If the catalyst in bed 4 is replaced with an equal volume of VK-701 and the inlet temperature is optimised to 407°C (765°F), the conversion can be further increased to 99.00%. This corresponds to a reduction of the stack gas SO_2 level by 20% compared to VK59 or 30% compared to VK48.

Bed 4			
Catalyst	**VK48**	**VK59**	**VK-701 LEAP5™**
Inlet temperature, °C (°F)	425 (797)	415 (779)	407 (765)
Outlet temperature, °C (°F)	428 (802)	418 (784)	411 (772)
Overall conversion, %	98.57	98.74	99.00
SO_2 in the stack, ppm	1390	1220	970

Table 1. Performance of VK-701 LEAP**5**™ in the final pass of a single-absorption plant when replacing VK48 or VK59 with an equal volume of VK-701.

Example 2: Reduced emissions from a double-absorption plant

The SO_2 emissions from an existing double-absorption plant can be reduced beyond the level of VK69 by also loading VK-701 LEAP**5**™ in the third pass.

Layout:	3:1 double-absorption plant
SO_2 source:	Burning of elemental sulphur
Feed gas:	11% SO_2, 10% O_2
Catalysts in beds 1/2:	VK38 / VK38
Conversion outlet bed 2:	88.5%

The performance of VK-701 and VK69 is compared to standard catalysts in Table 2. With standard potassium-promoted VK48 in bed 3 and VK38 in bed 4, the overall conversion of the plant is 99.85% corresponding to 200 ppm SO_2 in the stack gas. The feed gas to the fourth pass contains about 0.6% SO_2 in this case. If higher conversion is required, the first choice is to replace the VK38 in bed 4 with caesium-promoted VK69, which is optimised for the final pass of double-absorption plants, and reduce the inlet temperature to 395°C (743°F). This cuts the SO_2 emission to 100 ppm.

Bed 3			
Catalyst	**VK48**	**VK48**	**VK-701 LEAP5™**
Inlet temperature, °C (°F)	440 (824)	440 (824)	423 (793)
Outlet temperature, °C (°F)	461 (862)	461 (862)	447 (837)
Conversion outlet bed 3, %	95.45	95.45	96.43
Bed 4			
Catalyst	**VK38**	**VK69**	**VK69**
Inlet temperature, °C (°F)	425 (797)	395 (743)	395 (743)
Outlet temperature, °C (°F)	442 (828)	413 (775)	409 (768)
Overall conversion, %	99.85	99.92	99.95
SO_2 in the stack, ppm	200	100	64

Table 2. Performance of VK-701 LEAP**5**™ in the third pass of a 3:1 double-absorption plant.

A further reduction in SO_2 emission can be accomplished by replacing the VK48 in bed 3 with an equal amount of VK-701 LEAP**5**™ and operating the bed at an inlet temperature of 423°C (793°F). Due to the higher activity of the VK-701, the SO_2 content in the feed gas to bed 4 is reduced to 0.47%, and the overall conversion is increased to 99.95%. The 64 ppm SO_2 in the stack achieved with a combined VK-701/VK69 loading corresponds to a 36% reduction compared to the VK48/VK69 loading and as much as 68% reduction compared to a loading of conventional VK48/VK38 catalyst in beds 3 and 4.

For existing plants the reduced SO_2 emissions achievable with VK-701 provide an attractive alternative to investing in a caustic or hydrogen peroxide scrubber. Even for plants already equipped with tail-gas scrubbing, the VK-701 may be a cost-efficient way of reducing chemical consumption for the scrubbing.

VK-701 LEAP5™ operating experience

The first industrial installation of the VK-701 is in a single-absorption plant burning elemental sulphur located in the Western world. The SO_2 converter contains five catalyst beds with indirect cooling between beds 1 and 2 and quench air cooling after beds 2 and 3. No cooling is applied between beds 4 and 5. The feed gas to the converter contains 8.8% SO_2 and 12% O_2.

During a shutdown in 2010, the VK59 and VK48 catalysts in the final passes were replaced by equal volumes of VK-701 in order to cut SO_2 emissions and increase production capacity. Prior to installation of VK-701, the plant had been running at 245 MTPD (270 STPD) with about 420°C (788°F) inlet bed 4 and an overall conversion of 98.77% corresponding to about 1000 ppm SO_2 in the stack gas.

After start-up a test run was carried out during which analyses of SO_2 and O_2 were made and the temperature was measured at bed inlets and outlets. Multiple-point gas and temperature measurements revealed incomplete mixing of the quench air inlet bed 4, compromising performance significantly. However, similar measurements for the fifth bed indicated a more homogeneous gas composition.

The data obtained are reported in Table 3 alongside data from a comparable situation prior to the installation of VK-701 LEAP**5**™.

	Before installation of VK-701 LEAP5™	**After installation of VK-701 LEAP5™**
Catalyst loading in beds 4 and 5	12.0 m^3 VK59	13.4 m^3 VK-701
	13.2 m^3 VK48	13.0 m^3 VK-701
Production rate, MTPD (STPD)	245 (270)	266 (293)
Inlet temperature, bed 4, °C (°F)	420 (788)	404 (760)
Overall conversion, %	98.77	99.02
SO_2 in the stack, ppm	1005	720

Table 3. Improvement of conversion efficiency observed in a single-absorption plant by installing VK-701 LEAP**5**™ in the final passes.

After the installation of 26.4 m^3 VK-701 in the final passes and reduction of the inlet temperature to 404°C (760°F), the SO_2 concentration in the stack gas has been reduced to approximately 720 ppm at an increased production rate of 266 MTPD (293 STPD). Hence, by replacing VK59 and VK48 with the new VK-701 it is possible to reduce SO_2 emissions by 20% in terms of kg SO_2 per MT H_2SO_4 produced even at 9% higher production capacity. The observed activity of VK-701 is the double of new VK59 even with the mixing problems in bed 4.

Conclusion

Topsøe has responded to the demands placed on the sulphuric acid industry to lower SO_2 emissions by developing a new sulphuric acid catalyst designated VK-701 LEAP**5**™. The catalyst is based on our novel LEAP**5**™ technology which circumvents the transport deficiencies in the molten active phase of existing commercial sulphuric acid catalysts. The VK-701 contains two to three times as much active vanadium in the V^{5+} form compared to other commercial catalysts and, as a result, it offers exceptionally high activity at low temperature in converted strong gases.

SO_2 emissions from a typical 4-bed single-absorption sulphuric acid plant can be reduced by 20-30% by loading VK-701 in the final bed compared to a caesium-promoted catalyst or by 30-40% compared to a standard potassium-promoted catalyst. Emissions from the most efficient double-absorption plants can be further reduced by up to 40% when loading VK-701 in the third pass of a 3:1 plant and achieve down to 50 ppm SO_2 emission depending on feed gas and plant layout. Operating experience from a sulphur-burning single-absorption plant confirms the high activity of VK-701 LEAP**5**™.

Combining the high activities offered by VK-701 and VK69 presents opportunities for designing new 3:1 plants with as little as 20-50 ppm SO_2 in the stack gas (0.1-0.25 kg SO_2/MT H_2SO_4, 0.2-0.5 lbs/ST). For existing plants the reduced SO_2 emissions achievable with VK-701 provide an attractive alternative to investing in a caustic or hydrogen peroxide scrubber. Even for plants already equipped with tail-gas scrubbing, the VK-701 may be a cost-efficient way of reducing chemical consumption for the scrubbing.

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