race Davison’s laboratories test thousands of equilibrium fluid cracking catalyst (Ecat) samples each year. These samples provide important insights into FCC unit operations and are critical for unit optimization and troubleshooting.

The purpose of this article is twofold. First, it will communicate how Ecat activity, contaminants and other properties have shifted over the past ten years, both worldwide and by geographic region. Second, it will allow the individual refiner to rank their own FCC Ecat properties relative to the industry in several key categories.

The following data reflects ten years of Ecat sample analyses from 1997 through 2006. The data represents over 117,000 individual Ecat samples from approximately 300 FCC units around the world.

Figures 24 to 32 show a ten-year trend of average Ecat properties across all regions of the world: Asia Pacific (AP), European Union (EU), Latin America (LA) and North America (NA). EU includes Europe, Africa, the Middle East and Russia. North America includes the United States, Canada and the U.S. Virgin Islands. Data reflects Ecat samples
that we have received from 1997 through 2006, both from refiners using Grace Davison FCC catalyst as well as competitor products.

Figure 24 identifies interesting trends in MAT activity. All regions experienced significant increases in activity from 1997 through 2004, at which time activity stabilized. On a worldwide basis, average activity increased from 67.5 to 70.7 wt.% over the ten-year period. Additionally, North America has consistently reported the highest activity of the four regions, while Asia Pacific has seen the greatest overall gains, from 64.2 to 69.7 wt.%.

Higher activity is consistent with increases in Ecat rare earth content (Figure 25) and Ecat Unit Cell Size, UCS (Figure 26). Worldwide, average rare earth has climbed more than 65%, from 1.54 to 2.56 wt.%, over the past ten years. Similar increases are seen in each geographic region. Consistent with rare earth, average Ecat UCS data has seen a steady rise from 24.27 to 24.30Å.

Unit cell size and rare earth data suggests that the increase in Ecat activity is largely due to higher levels of rare earth exchanged onto the catalyst zeolite. Figures 25 and 26 also confirm conditions in the FCC Ecat that can lead to higher gasoline selectivity as a result of the shift to higher UCS Ecat. For many catalyst systems, this shift in UCS also suggests improved catalyst coke selectivity.

FCC catalyst alumina content has experienced a steady upward trend from 38.9 to 44.0 wt.%, as seen in Figure 27. Higher Al₂O₃ has been observed in all regions and confirms the industry's acceptance of the value of alumina content on FCC catalyst performance. Grace reported on the value of alumina-sol catalyst technologies in a recent Catalagram publication. ¹¹

Ecat contaminant trends are seen on Figures 28 to 32. Nickel in par-
ticular (Figure 28) provides insight into the differing FCC feedstocks processed in the Pacific Rim units as compared to the rest of the world. Vanadium (Figure 29) has been on the rise in the Asia Pacific region, increasing from 1900 to 2400 ppm and reflecting a 26% increase with a 14% increase in nickel. This trend is reversed on a worldwide basis, where vanadium has increased less than 6% while nickel is up almost 20% over the ten-year period, from 1475 to 1750 ppm. Nickel, and to a lesser extent vanadium, acts as dehydrogenation catalyst that increases the yields of the unwanted products hydrogen and coke. Vanadium is also mobile under FCC regenerator conditions and reduces catalyst activity by destroying zeolite framework.

Increased Ecatal activity together with higher nickel and vanadium levels suggest that today's catalysts have improved coke selectivity due to enhanced metals trapping and improved zeolite and matrix design.

Iron presents a mixed picture (Figure 30). Iron levels have dropped by 11% in Europe, 10% in Asia Pacific, and almost 5% in Latin America over the last ten years. Iron in North America, on the other hand, dropped significantly in the late 1990’s, but has been increasing steadily since 2000. Today the FCC’s with the highest Ecatal iron levels are located in North America. Organic based iron deposited on the catalyst during the cracking reactions can have a serious adverse effect on activity and bottoms cracking.

Calcium (Figure 31) had been stable for several years, but has climbed substantially since 2002. Worldwide CaO levels have increased 74% overall from 0.083 to 0.144 wt.%. Asia Pacific has the highest levels, while North and Latin America have seen the highest percentage increases. Europe has the lowest average calcium by weight percent and has also experienced the lowest percentage increase.
over the time period. Ca is often found on the surface of the Ecatalyst together with Fe and may be involved in the mechanism by which Fe poisons the Ecatalyst.\(^{(4)}\)

Sodium (Figure 32) has been trending downward on a worldwide basis, decreasing by over 12% since 1997. Asia Pacific and North America have contributed to the overall decrease by dropping almost 25% and 18%, respectively. Over the last ten years FCC units in Europe have the lowest levels of sodium, while Latin America has the highest. Sodium on Ecatalyst comes both from the raw materials used to manufacture the catalyst as well as salt contamination in the feedstock. Sodium can deactivate the catalyst by poisoning the acid sites on the matrix and zeolite and by surface area sintering.\(^{(5)}\)

Figures 33 through 42 present normal distributions of worldwide 2006 Ecatalyst data. These plots can be used as a quick reference to determine where an individual FCC unit falls versus the industry. The numbers atop each bar represent the number of FCC units within that data range.

As can be seen in Figure 33, MAT activity reflects a range from 57 to 81 with a mean of 70.7 wt.%. Most FCC units operating at an activity level greater than 77% likely process deeply hydrotreated feedstock, while units operating at lower activity could be processing residual based feedstocks and targeting lower conversion levels.

Figure 34 presents a rare earth range from 0.02 to 5.48 wt.% with a mean of 2.56 wt.% Many units operating at higher rare earth levels are taking advantage of Grace Davison’s IMPACT catalyst technology, which incorporates an integral rare earth vanadium trap. Figure 34 also confirms the limited number of units using a zero rare earth catalyst.
Alumina has a fairly broad range from 26.5 to 56.5 wt.%, with a mean of 44.0 wt.%, as can be seen on Figure 35.

Nickel and vanadium distributions are shown on Figures 36 and 37. While average Ecat vanadium levels are higher than nickel, nickel levels show a much wider distribution at the high end. Nickel ranges from a low of 22 ppm to several units with nickel levels greater than 12,000 ppm. The average nickel level worldwide is approximately 1750 ppm. Vanadium ranges from 40 to 7026 ppm, with a mean of about 1880 ppm.

Figure 38 shows the worldwide iron distribution. Like nickel, several units operate with a very high Iron content. The range is from 0.19 to 2.29 wt.% with a mean of 0.53 wt.%. Calcium reflects a range of 0.02 to 1.34 wt.% and a mean of 0.14 wt.%, as can be seen in Figure 39. Sodium distribution ranges from 0.09 to 0.95 wt.% (Figure 40). The mean is 0.30 wt.%. A normal distribution for total surface area is presented in Figure 41. Surface area indicates a range from 72 to 254 m²/g and a mean of 148 m²/g.

Figure 42 shows the distribution of the Ecatalyst 0-40 micron content, which ranges from 0 to 28 wt.% with a mean of 8 wt.%. The high end of the range indicates units, which can hold a tremendous amount of 0-40 material and perhaps generate additional fines from catalyst attrition. Several units at the low end of the distribution likely have cyclone problems, which limit their ability to hold particles less than 40 microns.

Data presented in this article confirms that the FCC industry values high activity catalysts for units that process hydrotreated feedstocks, are constrained by catalyst circulation and strive to operate at high conversion levels. Ecatalyst contaminant levels continue to increase, particularly CaO and Fe. As a result, the industry will continue to demand
Figure 36
Nickel Distribution

Figure 37
Vanadium Distribution

Figure 38
Iron Distribution
FCC catalysts that provide excellent coke selectivity and high liquid yields through enhanced metals tolerance. This data also confirms that there is a wide distribution of contaminant metals and that each catalyst application must be designed for the specific application.

References


