TRACE ELEMENTS OF PETROLEUM - FCCU FEEDSTOCK, FRESH, SPENT AND DEMETALLIZED FCCU CATALYST SOLIDS & LEACHATES; DEMETALLIZATION REDUCES LEACHABILITY, INCREASES STABILITY

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Trace elements contaminate Fluid Catalytic Cracking Unit (FCCU) catalysts by blocking pores and catalyzing steam deactivation. Elemental analyses of catalyst solids and leachates are necessary to characterize the system. Demetallization removes a portion of contaminants by pyrometallurgical and hydrometallurgical procedures. Catalysts were leached by various methods and IAW TCLP. Demetallized catalyst TCLP leachates are below the UTS TCLP limits proposed September 14, 1994, for all fourteen elements. Immediate catalytic activity improvement and improved resistance to steam deactivation is shown micro-activity (MAT) tests before and after severe steaming.

Fluid Catalytic Cracking is a valuable refining process to upgrade heavy hydrocarbons to high valued products (Avidan, 1993). Through the cycles of cracking, fresh catalyst deactivation is caused by contaminant blockage of active sites (nickel, vanadium, iron, et al.) and by steam catalyzed by contaminants, e.g. vanadium, sodium, et al. (Pine, 1990; Pavel, 1992). To compensate for decreased FCC feedstock conversion and product selectivity, a portion of the circulating catalyst equilibrium inventory is withdrawn for spent catalyst disposal, and fresh catalyst is added to the system (Habib, 1979).

Spent FCCU catalyst disposal quantities have been published in various formats, and disposition alternatives include those "options which recover metals: 1) On-site demetallization and recycle for FCCU catalysis -- on-site source reduction [13]; 2) Off-site demetallization and recycle for FCCU catalysis -- original application recycle [14]; 3) Off-site spent catalyst (ultra-low metals) sale to others [16] for further metals loading, a limited market at equilibrium which requires disposal by others and does not affect disposal of total replacement volumes of fresh catalyst sold, and the metals deposited from feedstocks. 4) Off-site demetallization for metals recovery prior to secondary use or disposal [17]; 5) Other waste treatment technologies prior to disposal, e.g. solidification, stabilization, vitrification, cementation, etc. [18]; 6) Cement kilns, with or without pretreatment, either 6a) cement kilns permitted/licensed for hazardous wastes, or 6b) cement kilns blending wastes as alternative feed stocks[16,19]; 7) Landfills [11,12,16,19]." (Pavel, 1995)

Trace elements enter the FCCU system from feedstocks, fresh catalysts, feedstock and/or catalyst additives. Analyses of petroleum by Filby, Yen, Shah, et al. (Yen, 1975), showed a wide range of elements in petroleum. The feedstock to FCCUs typically includes the gas oil fraction, between diesel and asphalt, and in some cases all of the long residue with a boiling point above diesel. Refiners normally analyze FCCU feedstock for C and S and occassionally N, for Ni and V fairly often, sometimes seldom analyze for more than Ni, V, and in some cases, Na, Fe. ICP elemental analyses for several feedstocks are shown in Table 1. Elemental analyses of spent Fluid Catalytic Cracking (FCC) catalyst solids and leachates are necessary to characterize the total FCC catalyst system including yield impacts and environmental considerations.

Catalyst and leachate analyses: Elemental analyses of solids and leachates were performed using ICP and XRF, analyses of leachates were performed by ICP. Table 2 shows a representative catalyst test set which includes a fresh, spent, and demetallized spent catalyst. Toxicity Characteristic Leaching Procedures (TCLPs) were performed in accordance with EPA standard methods, and results were compared to the proposed Universal Treatment Standards, Land Disposal Restrictions -- Phase II (LDRII), published September 19, 1994. Additional leach tests were performed with deionized water flushed (DIF) through catalyst using 20 parts water to 1 part catalyst. Demetallized catalyst TCLP leachates are below the UTS for all elements including vanadium (Pavel, 1994). New pyrometallurgical and hydrometallurgical controls and procedures further improve metal removal and enhance catalytic properties. Immediate activity improvement is seen in MATs prior to steaming. Improved resistance to steam deactivation, catalyzed by vanadium and other elements, is shown after spent and demetallized spent catalyst were steamed for 4 and 16 hours at 1450°F, and then ASTM microactivity (MAT) tested.

Demetallization processing (DEMET) takes a portion of spent FCC catalyst, removes a portion of metal contaminants by pyrometallurgical (calcining, sulfiding, nitrogen stripping, chlorinating) and hydrometallurgical (leaching, washing, drying) procedures, to return the base demetallized spent catalyst to the FCC. Standard demetallization has most frequently utilized 1450°F calcining and sulfiding with 650°F chlorinating. Off-gases from reactors are scrubbed (Elvin, 1993). Contaminant metals are precipitated and filtered for disposal in the same manner used for spent catalyst, or they can be shipped to a Best Demonstrated Available Technology recycler of metals, depending on the client preference or regulatory environment. The operation of one unit for one refiner has resulted in the recycle of over 15,000 tons of spent FCC catalyst back to the FCC. Demetallized spent FCC catalyst recycle has reduced the requirements for fresh catalyst additions and reduced generation of catalyst fines. DEMET processing removes contaminants known to be detrimental to conversion, product selectivities, and mechanical performance of the FCC. With DEMET capacity sized to reduce metals levels on circulating catalyst, yields could be improved due to lower metals on circulating catalyst.

New DEMET procedures improve metal removal, initial activity and hydrothermal stability. Standard DEMET processing utilizes a series of pyrometallurgical and hydrometallurgical procedures for metal removal. By removal of contaminants, access channels to active sites are renewed. Care is taken during processing to maintain the catalyst integrity and hydrothermal stability. New advancements in sulfidization and aqueous processing have further improved metal removal and demetallized spent catalyst characteristics of high initial activity, and low hydrothermal deactivation rates.

Table 1. FCCU Feedstock Elemental Analyses (ppm) by ICP

Element	Feed1	Feed2	Feed3	Feed4	Feed5	Feed6	Feed7
Aluminum	2.9	38.7	0.4	1.6	4.8	nt	0.5
Antimony	0.2	2.1	1.1	0.2	0.2	<0.2	<0.2
Barium	nt	nr	0.9	<0.1	<0.1	nt	<0.2
Beryllium	nt	nt	nt	nt	nt	nt	nt
Bismuth	0.6	bdl	<0.1	0.2	0.2	<0.2	<0.2
Boron	<0.1	4.3	<0.1	0.7	<0.1	nt	<0.2
Calcium	19.9	15.3	1.6	2.7	0.5	0.4	0.5
Carbon	nr	nr	1.4	7.8	4.4	2.2	4.8
Cerium	0.2	nr	<0.1	<0.1	<0.1	nt	nt
Chromium	0.6	nr	<0.1	<0.1	<0.1	<0.2	<0.2
Copper	0.2	0.4	0.2	0.1	<0.1	<0.2	<0.2
Iron	14.3	16.6	5.2	16.0	7.6	3.4	5.3
Lanthanum	0.1	nr	<0.1	<0.1	<0.1	nt	nt
Lead	0.3	2.4	0.1	0.3	0.6	<0.2	<0.2
Magnesium	2.5	3.5	2.6	1.0	0.1	0.2	0.3
Manganese	0.2	0.1	<0.1	0.1	<0.1	<0.2	<0.2
Neodymium	<0.1	nr	<0.1	<0.1	<0.1	nt	nt
Nickel	2.2	4.8	3.4	22.0	3.9	13.0	12.1
Phosphorus	0.7	2.3	0.6	0.1	0.2	<0.2	<0.2
Potassium	0.6	5.7	0.6	0.5	0.7	nt	<0.2
Praseodymium	<0.1	nr	<0.1	<0.1	<0.1	nt	nt
Selenium	nt	bdl	<0.1	0.2	0.2	nt	<0.2
Silica	nt	nt	nt	nt	nt	nt	nt
Sodium	21.4	27.4	1.4	28.0	1.2	2.1	0.5
Strontium	0.6	nr	<0.1	<0.1	<0.1	<0.2	<0.2
Sulfur	nr	nr	1.3	1.2	0.3	0.13	0.37
Tin	0.1	0.4	0.7	0.5	0.7	<0.2	0.8
Titanium	0.1	0.7	<0.1	0.1	<0.1	<0.2	<0.2
Vanadium	3.5	4.3	2.4	40.0	6.5	0.9	8.6
Zinc	0.9	2.6	0.4	1.2	0.3	nt	<0.2
Zirconium	<0.1	nr	0.1	<0.1	<0.1	nt	<0.2

note: "nt" indicates "not tested" at the time of that sample; "nr" indicates "not reported"

Improved metals removals are accomplished primarily during the pyrometallurgical steps of processing. Special DEMET procedures were developed by rigorous thermodynamic modeling of the sulfidizationenvironment to ensure the reaction mix and temperature appropriate to convert available contaminant oxides to sulfides (Pavel, 1993). Accurate analyses of all contaminant elements (not just nickel and vanadium) are required for accurate modeling. Improved metals removal enables more efficient utilization of hardware and provides the ability to lower metals on circulating catalyst. Improved metals removal shows that more sites have been uncovered, and micropore channels leading to active catalytic sites restored.

Elements not tested and/or reported in the following tables, but often found on catalysts include three groups. Elements most typical, but not tested and/or reported: Carbon, Chlorine, Hafnium, Hydrogen, Nitrogen, Oxygen, Scandium. The second group accounts for he rare earth mix supplied fresh catalyst manufacturers which includes the four reported plus Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Terbium, Ytterbium, Lutetium. The third group includes elements found in crude and on occassion various catalysts: Fluorine, Iridium, Osmium, Palladium, Platinium, Rhenium, Rhodium, Ruthenium. All tests have been performed by third party laboratories. The demetallization procedure used was for recycle of spent demetallized catalyst, alternative procedures would be utilized if processing for any other purposes. When some elements are removed, the elements remaining might appear to increase as a portion of the total remaining material. The list of elements is extensive, but not complete, as elemental testing includes over 70 elements.

Every FCCU feedstock, hardware, and catalyst system are unique. Some systems have more elements than in the following table (Table 2).

Improvements in hydrothermal stability and additional activity for recycle to the FCC are achieved through the hydrometallurgical processing steps. Special DEMET procedures were developed by rigorous modeling of solution properties during the wash step (Pavel, 1993). Additional proprietary steps are incorporated in the washing prior to drying on the belt filter. Aqueous processing modifications resulted in a number of attractive alternatives which can be selected through regulating variables in a single flexible design DEMET unit. For simplicity of graphic and tabular presentation, only one of the alternative advanced procedures is shown, it is labeled "special". Spent FCC catalyst was demetallized in the laboratory pilot plant. Microactivity and XRD testing were performed in accordance with ASTM standards. Steaming was performed at 1450°F 100% steam for 4 hours and 16 hours. The results prior to steaming and after 4 and 16 hours of steaming are shown in the Table 3 in comparison of the fresh, spent, standard demetallized, and special demetallized sample performance demonstrated by MAT testing.

Table 2. Fresh, Spent, and Demetallized Spent FCC Catalyst Solid and Leachate Analyses (ppm)

Elements Analyses by ICP	UTS LDRII TCLP	Fresh Catalyst Solid	Fresh Catalyst Leachates TCLP	Fresh Catalyst Leachates DIF	Spent Catalyst Solid	Spent Catalyst Leachates TCLP	Spent Catalyst Leachates DIF	Demetallized Spent Solid	Demetallized Spent Leachates TCLP	Demetallized Spent Leachates DIF	Element removal wt%spent
Aluminum	.....	142110	87.469	0.549	141190	114.813	2.961	175200	34.010	4.720	+24%
Antimony	2.1	246	bdl	bdl	1526	1.766	9.491	310	bdl	bdl	80%
Arsenic	5.0	215	0.223	bdl	250	1.495	bdl	96	0.113	0.205	62%
Barium	7.6	118	0.018	bdl	77	0.667	0.014	52	0.329	0.060	32%
Beryllium	0.014	3	0.006	0.002	38	0.368	0.509	10	bdl	0.014	74%
Bismuth	.....	bdl	bdl	bdl	7	0.319	0.015	bdl	bdl	bdl	bdl
Boron	.....	20	0.029	0.021	20	0.109	0.094	14	0.067	0.037	30%
Cadmium	0.19	4	bdl	bdl	20	bdl	bdl	30	bdl	bdl	-55%
Calcium	.....	1372	7.059	0.278	1819	1.889	0.283	961	4.061	1.084	47%
Cerium	.....	4682	13.183	0.085	1171	14.915	0.065	1264	26.627	3.481	+ 8%
Chromium	0.86	675	0.043	0.011	586	bdl	bdl	579	bdl	bdl	-16%
Cobalt	.....	8	bdl	bdl	193	0.013	0.013	12	0.142	0.052	93%
Copper	.....	9	0.013	0.009	29	0.103	0.002	9	0.012	0.001	69%
Iron	.....	3053	0.219	0.016	4292	0.328	0.301	902	2.320	0.053	79%
Lanthanum	.....	3518	8.401	0.017	2757	46.975	0.246	2782	57.195	8.928	+1%
Lead	0.37	27	bdl	bdl	38	bdl	bdl	bdl	bdl	bdl	~99%
Lithium	.....	42	0.054	0.007	56	0.431	0.314	32	0.385	0.285	43%
Magnesium	.....	316	2.041	0.106	62	0.827	0.094	33	0.844	0.333	47%
Manganese	.....	12	0.055	0.001	12	0.052	0.001	8	0.036	0.012	33%
Mercury	0.020	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Molybdenum	.....	8	0.016	0.011	14	0.227	0.474	4	0.058	bdl	71%
Neodymium	.....	2303	8.914	0.036	1703	20.987	0.192	1182	31.298	3.293	31%
Nickel	5.0	33	0.049	0.006	3432	1.868	0.269	153	1.745	0.547	96%
Potassium	.....	890	2.801	0.348	281	1.205	0.224	242	0.097	0.012	16%
Presodymium	.....	587	1.991	bdl	432	6.347	bdl	381	9.512	1.071	11%
Selenium	0.16	11	0.046	bdl	10	0.040	bdl	bdl	bdl	bdl	~99%
Silicon	.....	310010	68.917	8.428	310485	50.384	32.506	282500	55.571	8.440	9%
Silver	0.3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Sodium	.....	3178	62.518	12.795	2283	26.993	16.473	2211	16.367	12.147	3%
Sulfur	.....	2973	84.625	61.931	446	1.134	0.882	2357	86.837	13.326	+428%
Thallium	0.078	92	0.047	0.032	60	0.867	0.353	bdl	bdl	bdl	~99%
Tin	.....	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Titanium	.....	4170	0.064	0.029	7550	0.016	0.165	3800	0.264	0.016	50%
Vanadium	0.23	63	0.137	0.160	4967	48.437	68.500	1176	0.123	0.187	76%
Zinc	5.3	91	0.537	nt	136	0.162	bdl	95	1.360	0.098	30%

Analyses by XRF		Fresh Catalyst solids only	Spent Catalyst solids only	Demetallized Spent solids only	Element removal wt%spent
Bromine	.....	< 0.4	< 0.4	< 0.4	NoChange
Cesium	.....	< 7.5	22.3< 7.5	22.3< 7.5	NoChange
Gallium	.....	28.6+/- 1.0	53.2+/- 2.0	29.7+/- 2.0	44%
Germanium	.....	< 0.7	2.1+/- 0.5	< 1.0	~99%
Indium	.....	< 0.6	< 1.8	< 1.8	NoChange
Iodine	.....	9.4+/- 2.8	22.5+/- 4.0	10.3+/- 3.0	54%
Niobium	.....	13.7+/- 1.0	25.3+/- 1.0	9.9+/- 0.8	61%
Phosphorus	.....	653.0+/-38.0	666.0+/-37.0	604.0+/-31.0	9%
Rubidium	.....	3.6+/- 0.5	2.9+/- 0.6	1.7+/- 0.6	41%
Strontium	.....	60.5+/- 1.0	67.5+/- 1.0	60.6< 1.4	10%
Tantalum	.....	< 4.9	< 8.0	< 8.0	NoChange
Tellurium	.....	< 1.4	< 2.5	< 2.5	NoChange
Thorium	.....	6.7+/- 1.0	18.7 < 1.0	16.8+/- 1.0	10%
Tungsten	.....	<3.1	< 18.9	< 18.9	NoChange
Uranium	.....	2.7+/-1.0	4.1+/- 1.1	3.2+/- 1.1	22%
Yttrium	.....	59.8+/-1.0	32.6+/- 1.0	27.4+/-1.0	15%
Zirconium	.....	103.0+/-1.0	125.0+/- 2.0	125.0+/- 2.0	NoChange

Note: bdl = below detection limit; nt=not tested; ~99%=removal to below detection limits.

Table 3. Fresh, Spent, Standard Demetallized, and Special Demetallized Spent Catalyst

	Fresh without DEMET	ECAT without DEMET	DCAT after Standard DEMET	DCAT after Special DEMET
MAT yields prior steaming, wt%				
Conversion	94.29	55.55	67.74	70.78
2nd Order Conversion	16.50	1.25	2.10	2.42
Gasoline/Conversion	0.27	0.63	0.56	0.54
2ndOrderConversion/Coke	0.79	0.15	0.24	0.21
Dry Gas/2ndOrderConversion	0.38	1.55	1.23	1.03
LCO/LCO+Slurry	0.47	0.52	0.60	0.63
Hydrogen	0.29	0.46	0.26	0.46
Dry Gas (C1+C2s)	6.22	1.93	2.57	2.50
Propane	17.06	0.85	2.30	1.74
Propylene	2.17	2.74	4.34	4.84
Isobutane	14.36	2.28	6.17	5.60
Normal_Butane	6.65	0.56	1.35	1.22
Isobutene	0.39	0.93	0.96	1.17
Total Butenes	1.21	3.24	3.91	4.51
Gasoline (C5-430F)	25.41	34.98	38.10	38.34
LCO (430-650F)	2.66	22.94	19.36	18.55
Slurry (650F+)	3.05	21.51	12.91	10.68
Coke	20.91	8.51	8.74	11.56
MAT yields after 16 hours steaming, wt%				
Conversion	62.91	35.86	40.38	56.56
2nd Order Conversion	1.70	0.56	0.68	1.30
Gasoline/Conversion	0.66	0.56	0.65	0.68
2ndOrderConversion/Coke	0.37	0.07	0.14	0.45
DryGas/2ndOrderConversion	1.11	2.98	2.55	1.37
LCO/LCO+Slurry	0.68	0.33	0.37	0.52
Hydrogen	0.07	0.64	0.34	0.21
DryGas (C1+C2s)	1.88	1.67	1.72	1.78
Propane	1.19	1.01	0.66	0.79
Propylene	4.22	1.73	2.21	3.97
Isobutane	3.94	0.54	0.95	2.54
Normal_Butane	0.82	0.19	0.28	0.51
Isobutene	1.17	0.63	1.19	1.99
Total Butenes	4.77	1.63	3.17	5.70
Gasoline (C5-430F)	41.47	20.18	26.22	38.20
LCO (430-650F)	21.36	20.89	21.92	22.47
Slurry (650F+)	15.73	43.25	37.70	20.98
Coke	4.56	8.28	4.83	2.87

Demetallized spent FCCU catalyst TCLP leachate is below the proposed LDR-II UTS for all 14 elements. Demetallization for primary recycling to FCCUs can reduce fresh catalyst additions, reduce circulating inventory metals (or hold a metals level with increasing feed stock metals), and reduce leachable metals for a portion of spent catalyst withdrawn. Contaminant metals are controlled in FCCUs due to their deleterious affects on conversion, selectivity, and deactivation of fresh catalyst. Similarly, cement kiln blends are limited to a kiln blend of 83 ppm vanadium due to potential problems with refractories (Petrovsky, 1994). For those kilns not already at a vanadium limit due to vanadium content of the local quarry supply, the dilution of vanadium sets the limit of spent FCCU catalyst processed to 1-2% of kiln feed stock. The mobility of vanadium is well known in refining, and it appears the conditions of cement kiln processing do not limit vanadium mobility. Demetallization could be used to reduce the leachable metals prior to secondary recycling (cement kilns, etc.) or disposal. Using DEMET to remove vanadium from feed stocks to cement kilns would increase capability to substitute spent FCCU catalyst in the kiln blend." (Pavel, 1995)

Conclusion. Demetallization reduces the leachability of contaminant elements measured by TCLP and de-ionized water flushes. After demetallization of spent FCCU catalyst all fourteen TCLP leachate elements are below the proposed LDR-II Universal Treatment Standard levels. For every indicator of catalyst performance after severe steaming, standard demetallization appears superior to equilibrium catalyst without demetallization, and special demetallization appears superior to standard demetallization and far superior to equilibrium catalyst without demetallization. Graphs show higher conversion, and higher gasoline yields with lower coke for special demetallized catalyst compared to equilibrium catalyst. The graphs also show the special demetallized catalyst performance ratios are also superior with lower dry gas/kinetic conversion ratios, higher gasoline/coke ratios, higher gasoline/conversion selectivities, higher light cycle oil selectivities, higher dynamic activities, as well as increased C3 and C4 olefins and isobutylene. DEMETallization appears very well suited for the marketplace of new gasolines and higher middle distillate demands. The special DEMET process significantly increases the activity, selectivity and hydrothermal stability of the catalyst and minimizes the fresh catalyst required to maintain FCCU activity.

References:

Avidan, A. A. (1993). Origin, development and scope of FCC catalysis, J. S. Magee and M. M. Mitchell, Jr., Eds., Fluid Catalytic Cracking: Science and Technology, Studies in Surface Science and Catalysis, Vol. 76, (Amsterdam, Elsevier) 1.

Elvin, F. J. and Pavel, S. K. (1993). Commercial Operations of a DEMET Unit, NPRA Annual Meeting #AM-93-54.

Federal Register (1994), 40 CFR Parts 148, et al. Land Disposal Restrictions Phase II -- Universal Treatment Standards, and Treatment Standards for Organic Toxicity Characteristic wastes and Newly Listed Wastes; Final Rule, Sep. 19, 1994.

Habib, T. H. and Venuto, P. B. (1979). Fluid Catalytic Cracking with Zeolite Catalysts, (NY, NY: Marcel Dekker).

Pavel, S. K. (1992). The deactivating effects of vanadium and steam are compared for fresh, equilibrium, and demetallized catalyst. AIChE Annual Meeting, Miami, FL.

Pavel, S. K., and Elvin, F. J. (1993). Minimization of Petroleum Refinery Waste by Demetallization and Recycling of Spent FCCU Catalyst, Hager, J., Hansen, B., Imrie, W., Pusatori, J., and Ramachandran, V., eds., Extraction and Processing for the Treatment and Minimization of Wastes, The Minerals, Metals & Materials Society, WDC, 1015.

Pavel, S. K. and Elvin, F. J. (1994). Elemental Analysis of FCCU catalysts: Fresh, Equilibrium, and Demetallized, Symposium on Recent Advances in FCC Technology, AIChE Spring National Meeting, Atlanta, GA.

Pavel, S. K. and Elvin, F. J. (1995). Fresh, Spent and Demetallized Spent FCCU Catalysts Characterized by Detailed Elemental Analysis of Powder and Leachate", Symposium on New Techniques in Materials and Catalyst Characterization Preprints, ACS, Division of Petroleum Chemistry, Washington, DC. 198.

Pavel, S. K. and Elvin, F. J. (1996). New New FCCU DEMET® Process to produce demetallized spent catalyst with high activity and low hydrothermal deactivation rates. NPRA Annual Meeting, #AM-96-45.

Petrovsky, J. (1994). Question & Answer Session on Waste Issues", 1994 NPRA Refinery & Petrochemical Plant Environmental Conference (Washington, D. C., National Petroleum Refiners Association).

Pine, L. (1990). Vanadium-Catalyzed Destruction of USY Zeolites, J. Catal., 125, 514.

Yen, T. F., ed., (1975). The Role of Trace Metals in Petroleum, (Ann Arbor, MI: Ann Arbor Science Publishers, Inc.).