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Metal recovery and rejuvenation of metal-loaded spent catalysts

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Abstract

Metal recovery and/or rejuvenation technologies of the spent catalysts resulting from various sources are reviewed. The fluid cracking catalyst (FCC), resid fluid cracking catalyst (RFCC), hydrodesulfurization (HDS) catalyst, supported and unsupported precious metal containing catalysts, i.e., reforming catalyst, auto catalyst and other catalysts from a variety of industrial processes are targeted. The precious metal recovery technologies such as the processes using aqua regia, chlorination, segregation and Rose (metallurgical) method are discussed in detail. A series of the FCC demetalation/regeneration processes such as Met-X, Demet, Demet II, Demet III and Demet IV is also described from the view point of the developmental history. Two physical processes using the high gradient magnetic and density grading separator are also reviewed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Metal recovery; Catalyst rejuvenation; Recycle; Precious metals; Demet process

1. Introduction

The principal metal contaminants in various crudes produced today are nickel and vanadium. A large portion of these metals is present as organometallic chelates with a planar porphyrin structure [1]. Under the fluid catalytic cracking (FCC) operating conditions, almost 100% of these metal contaminants decomposes and deposits on the FCC catalyst surface [2]. The most FCC feeds such as the Venezuelan Largamedio crude contain V considerably higher than Ni. The manner in which V is deposited on the catalyst surface, and the deleterious effect that V has on cracking catalyst performance distinctly differ from those of Ni. An artificial deposition of the benzene solution of naphthenates of Ni and V on alumina, silica, zirconia, magnesia, and titania showed that V preferentially deposits on basic oxides and Ni on acidic oxides [3].

Studies for deposition of these metals on the catalyst with secondary ion mass spectroscopy (SIMS) [4], X-ray photoelectron spectroscopy (XPS) and atomic absorption spectrophotometry [5], electron probe microanalysis (EMPA) and differential thermal analysis [6,7] also show that nickel is in general homogeneously distributed throughout the catalyst surface, but vanadium is preferentially deposited on the zeolite sites and interacts destructively under the cracking condition. Consequently, vanadium oxide interacts with rare earth metals exchanged with the zeolite sites to form an eutectic mixture to cause severe loss of catalytic activity. It has been known that the eutectic mixture formation is promoted by an alkaline metal. On the other hand, Ni is primarily

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responsible for promoting the dehydrogenation activity which produces coke and gaseous products, in particular, hydrogen and methane at the expense of desired liquid products.

The interaction of Ni and V on the basic components of FCC catalyst such as clay, amorphous aluminosilicates and zeolite has been studied by XPS [8]. It showed that Ni interacted with the clay and silicate gel to form $NiAl_2O_4$, and $NiSiO_3$-like compound with the migrated silica, respectively. The zeolite component is not affected by Ni. On the other hand, Laser Raman spectroscopy, XPS and XRD results have indicated that steaming in the presence of even a small amount (<1.0%) of V cause the collapse of the zeolite structure with total loss of catalytic activity due to the formation of $CeVO_4$, mullite, $Al_6Si_2O_{13}$, and tridymite, and that SiO_2 interacts with the rare earth exchanged Y zeolite [9]. Also Pine has published a paper dealing with vanadium-catalyzed destruction of US Y-zeolite [10]. In the presence of steam (760°C, 1 atm), V on the catalyst surface form volatile compounds such as H_4VO_4 and $H_4V_2O_7$ capable of migrating from catalyst particle to particle [11]. This migrating V can be adsorbed by Mg–silicate [11] and alumina [12], which are capable of forming a stable and innocuous vanadate.

Besides FCC and resid fluid crcking catalyst (RFCC), many types of spent catalysts have been produced in the petroleum refining and the production of petrochemicals, commodity and fine chemicals including pharmaceutical, and catalytic converters of automobiles. These spent catalysts have been discarded for landfill in the past, but environmental pollution of air, soil and ocean contaminated by these waste catalysts has become a serious global problem. It is certain that some of them may soon be classified as a hazardous toxic waste, which will require an additional treatment to comply with the strict control for handling and disposal. In short, the spent catalyst wastes have become an environmental problem, and at the same time, it has presented an opportunity for a new business to rejuvenate, recycle and convert the spent catalyst to an environmentally acceptable safe material for recycle. The catalyst recycling of the spent FCC, RFCC, HDS, supported and homogeneous precious metal catalysts and three way auto catalysts became the main concern of the catalyst users as well as manufacturers.

2. FCC catalysts

According to the statistics compiled in the US in 1991, the new catalyst demand and the resulting catalyst waste were 190,000 and 120,000 t/year, respectively. Among the waste catalyst, 53,000 t were discarded with a cost of $190/t, 42,000 t were consumed for the cement production with the handling cost of $110/t, and approximately 20,000 t were recycled to the FCC unit at the price of $200–400/t [13]. In Europe, half of 60,000 t of the FCC/RFCC waste was discarded, while 105,000 t of the same catalyst waste was produced in Japan in 1991. About 65% of this waste was reutilized as the raw material for cement and ceramic industry, and 25% was used for the waste water filtering agent, the soil improver, asphalt and lagging material. The rest (10%) was discarded.

As shown in Table 1. the total quantity of the spent catalyst withdrawn from the FCC/RFCC units alone reached about 160,000 t/year worldwide in 1993. The catalyst demand of FCC and RFCC catalyst has rapidly grown due to an increase in the newly installed RFCC units, and are estimated to be 477,000 t/year in 1996, and 545,000 t/year in 1998 [13], and the spent catalysts would be roughly 300,000 t/year in 1996 and 370,000 t/year for 1996 and 1998, respectively, assuming that 63–68% of the catalyst will ultimately wind up as the spent catalyst. In the past, the metal-deposited FCC catalyst was replaced with fresh or equilibrium catalysts in order to control the metal levels of the catalyst inventory for the refinery FCC

Table 1
Worldwide demand of FCC/RFCC catalyst[a]

Country	FCC/RFCC catalyst demand (metric t/year)			
	Year			
	1993	1994	1996	1998
USA, Canada	230,000	235,000	250,000	275,000
Middle South America	31,000	33,000	40,000	45,000
Asia–Pacific	47,000	57,000	86,000	117,000
Japan	22,000	26,000	33,000	34,000
Others	25,000	31,000	53,000	83,000
Europe	80,000	82,000	86,000	90,000
Others	12,000	13,000	15,000	18,000

[a] Except China.

operation. When these are classified as a toxic hazardous material, the currently available options are no longer viable.

In order to reduce the catalyst cost as a FCC catalyst user, Atlantic Refining Company and Sinclair Oil company independently developed Met-X [14–16] and Demet process [17–25], respectively, and commercially used in their own refineries at Philadelphia, PA and Woodriver, IL in 1960s, respectively. These operations were ceased at the advent of the zeolite catalyst. When Atlantic Refining and Richfield Oil were merged to become Atlantic Richfield, and then further merged with Sinclair Oil to become Atlantic Richfield in 1969, new generations of Demet process such as Demet II (called Demet-X in some cases), Demet III [26–36] and Demet IV [37] were developed in 1970s and commercialized later.

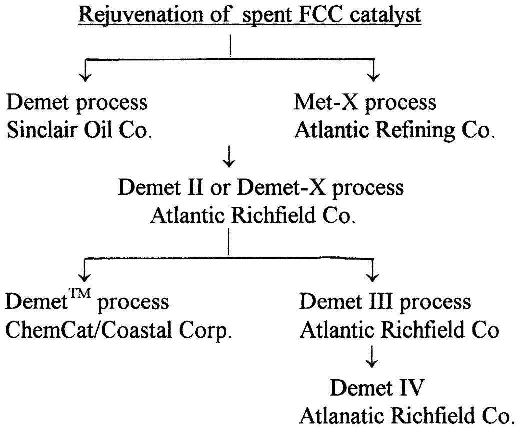


Fig. 1. New generations of FCC Demet processes.

In the Met-X process, the metal contaminants deposited on the amorphorous cracking catalyst was activated under H_2, and the resulting activated metals were removed in an acidic aqueous medium with an ion exchange resin. This process was operated in a 40 t/day unit in connection with a 30,000 b/day Orthoflow cracking unit at the Philadelphia refinery of Atlantic Refining in 1960s. On the other hand, Demet process was consisted of three steps, sulfiding the metal contaminants with H_2S, the reductive chlorination of the resulting metal sulfides, and washing the metal chlorides remained on the catalyst off the catalyst matrix. It was also commercially applied at the Woodriver refinery, Woodriver, IL by Sinclair Oil Corporation in the 1960s.

One nice feature of the Met-X process was incorporated into the Demet process, and was named as Demet II or Demet-X process in some cases at the early stage of Demet process development at Atlantic Richfield in 1970s [38]. The demetalated/rejuvenated catalyst by the Demet process was dried and blended in the FCC feed oil and the blend was directly sent to the cracking unit, which was a key feature practiced in the Met-X process. The fundamental chemistry involved in these two processes, Demet and Demet II, was altered to develop new generations of the demetalation processes, i.e., the Demet III and Demet IV process, to make it applicable to the zeolite containing FCC catalyst, and to allow it to become easier to comply with the environmental regulations. The commercial viability of Demet III process was demonstrated by the extensive pilot plant work at Atlantic Richfield, and later this Demet technology was sold to the ChemCat Corporation in 1985, and currently the commercial process known as Demet™ is offered by the ChemCat and Coastal Corporation since 1990 [39]. The developmental history of Demet processes for regeneration of the FCC catalyst is shown in Fig. 1.

Demet II process is consisted of three main steps, e.g., sulfidation, reductive chlorination, and washing. The flow diagram of Demet II process is illustrated in Fig. 2. The high metal containing equilibrium FCC catalyst comprised zeolite shown below was selected for the experiment of metal removal/rejuvenation runs via the Demet processes.

	Catalytic activity			Surface area, m^2/g	
	MA	CPF	H_2/CH_4	N_2	Zeolite
Virgin catalyst	80	0.75	8.0		
Metal contaminated catalyst	59	3.01	20.0	104	29

MA: microactivity, CPF: coke-producing factor, H_2/CH_4 ratio in gaseous product produced in the MA test (see Appendix A).

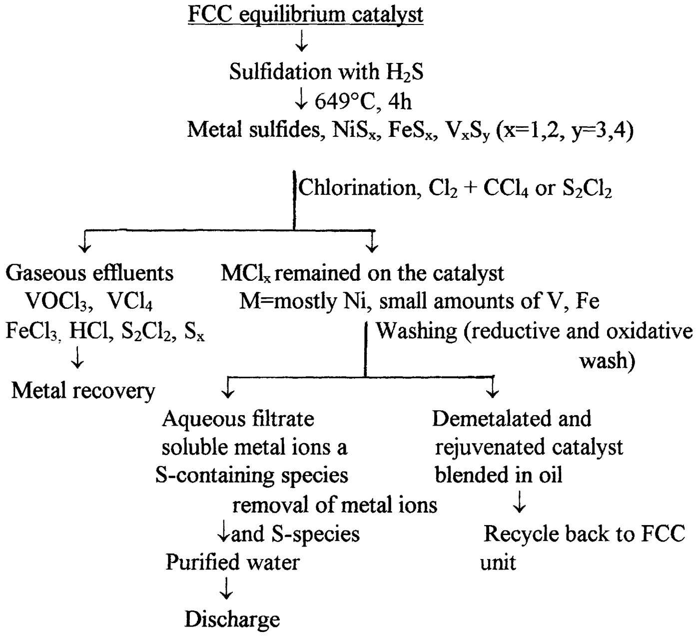
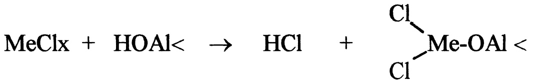


Fig. 2. Demet II process flow diagram.

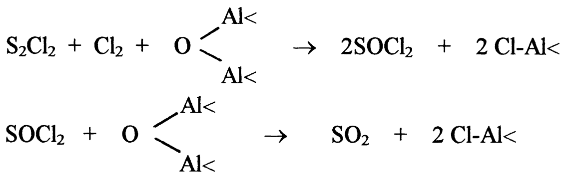
In the chlorination reaction of the FCC equilibrium catalyst with Cl_2 alone, no volatile chlorides of Fe or V were produced, and thus, these volatile chlorides were not found in the gaseous reaction effluent. However, both HCl and SO_2 were observed in the effluent gas. The $NiCl_2$ formed and remained on the catalyst surface was removed along with other nonvotalitle metal chlorides in the subsequent washing step.

$$NiS + Cl_2 \rightarrow NiCl_2 \downarrow + S_2Cl_2$$
$$FeS \text{ or } FeS_2 + Cl_2 \rightarrow FeCl_3 \downarrow + S_2Cl_2$$
$$V_2S_3 \text{ or } VS_x + Cl_2 \rightarrow VCl_4 \downarrow + S_2Cl_2$$

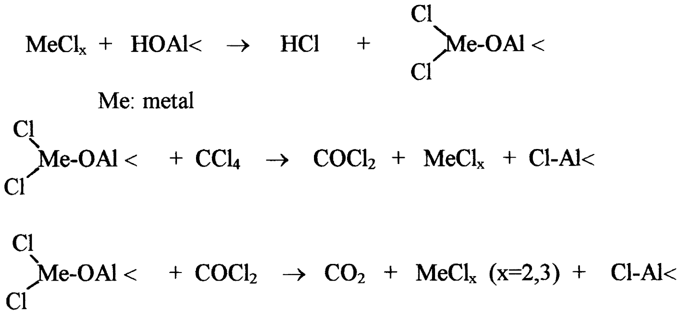
However, chlorination with Cl_2 with a promoter (S_2Cl_2 or CCl_4) produced volatile chlorides $VOCl_3$, VCl_4, and $FeCl_3$. Major effluent gas components were VCl_4, $VOCl_3$, $FeCl_3$, HCl, S_x, unreacted Cl_2, and oxidized and unreacted promoter. At the same time, Ni was converted to $NiCl_2$, which remained on the catalyst surface, and was washed out in the subsequent washing. The presence of HCl and SO_2 in the effluent gas can be explained by the following reactions of metal chlorides with the hydroxy group on the alumina surface. Apparently no volatile metal chlorides are observed because of inability of free Cl_2 without a promoter to break the metal–O bond.


$$MeClx + HOAl< \rightarrow HCl + (Cl)_2{>}Me\text{-}OAl<$$

As long as active hydroxyl groups are not present on the catalyst surface, it is unlikely that volatile metal chloride will be formed. The presence of SO_2 in the effluent gas may be attributable to the reaction of S_2Cl_2 (a promoter) with the alumina surface.


$$S_2Cl_2 + Cl_2 + O(Al<)_2 \rightarrow 2SOCl_2 + 2\,Cl\text{-}Al<$$
$$SOCl_2 + O(Al<)_2 \rightarrow SO_2 + 2\,Cl\text{-}Al<$$

It is also believed that CCl_4 serves as a reducing (promoting) agent in order to free the metal chlorides from the alumina surface in the chlorination with Cl_2 and CCl_4:



$$\mathrm{MeCl_x + HOAl{<} \rightarrow HCl + (Cl)_2{>}Me\text{-}OAl{<}}$$

Me: metal

$$\mathrm{(Cl)_2{>}Me\text{-}OAl{<} + CCl_4 \rightarrow COCl_2 + MeCl_x + Cl\text{-}Al{<}}$$

$$\mathrm{(Cl)_2{>}Me\text{-}OAl{<} + COCl_2 \rightarrow CO_2 + MeCl_x\ (x=2,3) + Cl\text{-}Al{<}}$$

In order to avoid the handling and disposal problem of the gaseous reaction effluent comprised $VOCl_3$, VCl_4, $FeCl_3$, HCl, S_2Cl_2 and S_x, and the aqueous washing solution containing metal chloride and soluble S-moieties generated in Demet II as illustrated in Fig. 2, the reductive chlorination step in the process was replaced with a simple air oxidation reaction in the Demet III process.

The metal sulfides resulting from the first step are oxidized to readily washable moieties such as sulfate, thiosulfate and dithionate by the air oxidation reaction, which are subsequently washed off the catalyst by a combination of reductive wash with SO_2 saturated solution and oxidative wash with an aqueous H_2O_2 solution. The flow diagram of the Demet III process is shown in Fig. 3.

For purifying the resulting aqueous filtrate containing metal ions and soluble S-species to meet the environmental specifications for clean water, there has been suggested various treating methods with a base such as lime and caustic soda. Ion exchange resins could also be used for the same purpose. General Electric developed a process to extract metal ions by utilizing membrane technology. The process strips dissolved metals (Cu, Zn, Ni, Cd, Cr, W, etc.) from inustrial wastewater by routing the process streams through thousands of hollow fibers, each with an internal diameter of about 200 μm (through 0.05 μm fiber pores) in a continuous manner. This process uses two compact modules. In the stripping module, the metals ions are continuously removed as the aqueous stream flows through the system. The other module produces concentrated metal-containing solutions. For stripping metal ions, a special solution containing an acid, salt, or base, solvent, complexing agent is employed. For example, hydroxyoximes are used for Cu ions [40].

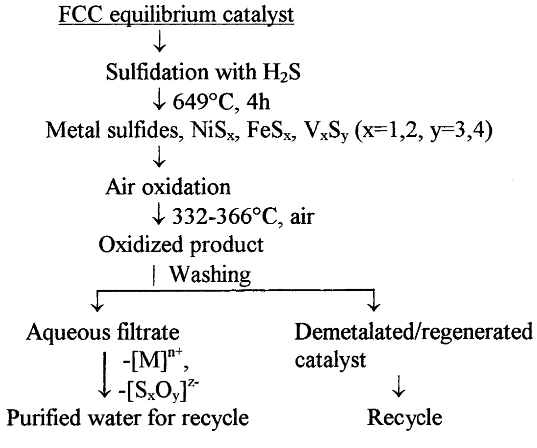


Fig. 3. Flow diagram of Demet III process.

Further efforts led to the Demet IV process [37], which was consisted of two steps, namely, air calcination with or without steam followed by the simple wash. This is the simplest process, which is specially suited for regenerating the catalyst resulted from processing the high vanadium feed. In Demet IV, only vanadium was activated as V_2O_5 in a discrete phase separated from the catalyst matrix by the air calcination at an elevated temperature. The resulting V_2O_5 was readily dissolved in water or alcohol such as methanol and ethanol. The trace amount of vanadium remained on the catalyst was further washed with a combination of a reductive wash with an SO_2 saturated solution and an oxidative wash with an aqueous H_2O_2 solution. The extent of vanadium activation depends on the calcination temperatures, i.e., the higher the calcination temperature, the more vanadium was activated and can be removed by a simple washing (see Fig. 4). The effect of calcination time and the partial pressure of oxygen on the extent and rate of vanadium

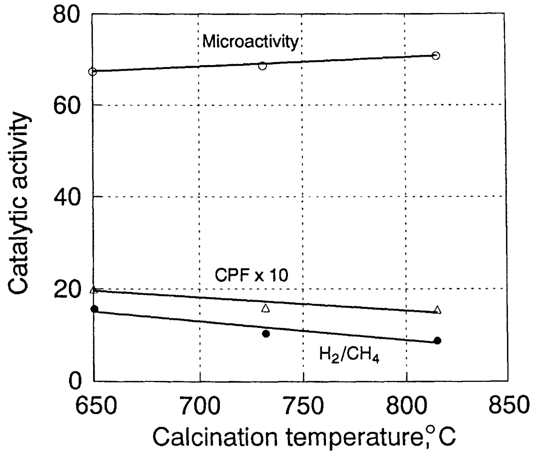


Fig. 4. Catalytic activity vs. calcination.

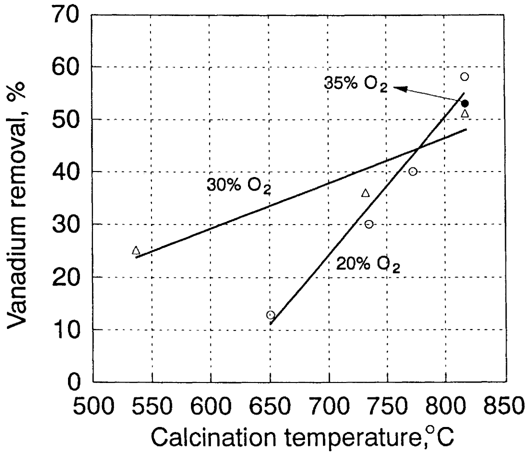


Fig. 6. V removal vs. O_2 partial pressure.

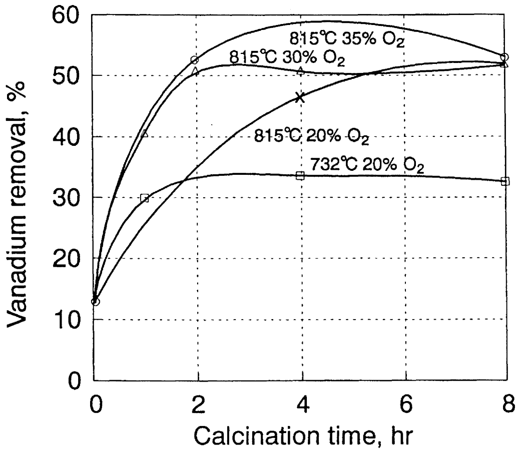


Fig. 5. V removal vs. calcination temperature time.

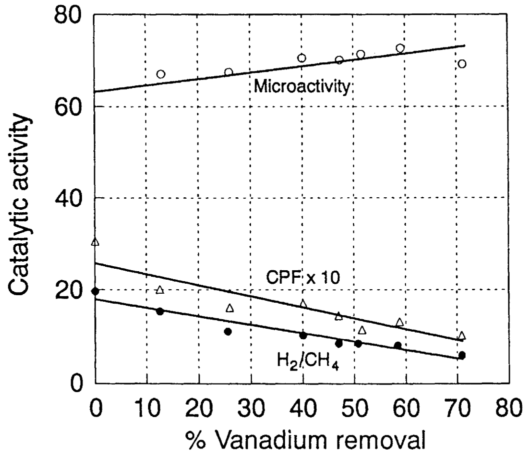


Fig. 7. Catalytic activity vs. V removal.

activation at a given temperature are shown in Figs. 5 and 6, respectively. The catalytic activity of devanadated catalyst is correlated with the extent of vanadium removal in Fig. 7 and Table 2.

The procedure of calcinating the FCC equilibrium catalyst in air at 750°C followed by reductive washing was repeated with devanadated catalyst resulting from previous cycle.

Approximately, 70% of vanadium on the catalyst was removed by repeating three successive runs while both Ni and Fe remained intact [37]. One can readily conclude that nearly 90% of the virgin catalyst activity can be restored by removing vanadium alone by Demet IV process.

Table 2
Successive vanadium removal by Demet IV

Cycle no.	% V removed	Catalytic activity		
		MA	CPF	H_2/CH_4
Catalyst sample	7300 ppm[a]	59.1	3.02	20.0
Virgin catalyst	0	80.0	0.75	8.0
Devanadated catalyst				
1	47	70.9	1.40	8.70
2	59 (23[b])	72.9	1.28	8.64
3	71 (29[b])	69.8	1.11	7.14

[a] V content.

[b] % based on remaining V.

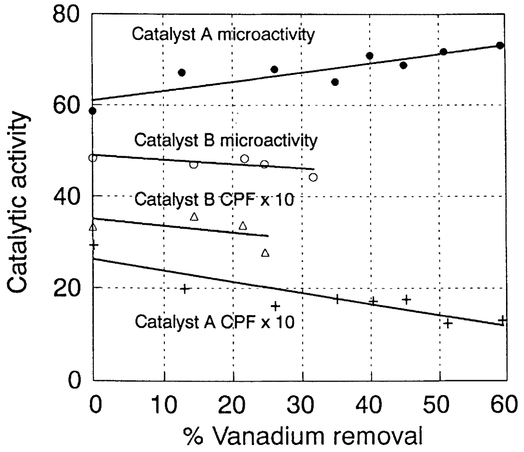


Fig. 8. Comparison of catalyst A and B, catalytic activity vs. V removal.

Besides these factors, the effect of this process greatly depend on the nature of the catalyst matrix whether or not it is metal tolerant. The results are shown in Fig. 8.

The catalytic activity of the devanadated catalyst by Demet IV was fully rejuvenated to the comparable level to that of the demetalated (Ni, Fe, V) catalyst obtained by the Demet III process. In the Demet III process, metal contaminants such as Ni, Fe and V were removed, and the resulting demetalated catalysts was effectively rejuvenated. The demetalation procedure remarkably improved the catalytic activity, which was close to that of the virgin catalyst. The representative results of these processes are compared in Table 3. In short, the extent of the catalyst rejuvenation by Demet IV was as good as that of Demet III. These observations lead to cast a doubt on the conventional belief that V deposited on the FCC catalyst destroys the zeolitic structure permanently through strong interactions as reported in the literature.

In the Demet^{TM} technology, the commercial scale results of the FCC demetalation [41–47], deactivation rate of the demetalated FCC catalyst [48], long term effects of FCC unit catalyst demetalation [49], and commercial operations of a Demet unit [50] have been reported. The 10 t/day off site pilot plant was constructed for the process by ChemCat Corporation, and approximately 70–80% of Ni and 30–40% V were removed from the equilibrium FCC catalyst. The flow diagram of ChemCat's Demet process is shown in Fig. 9 [51]. The FCC equilibrium catalyst was regenerated by demetalation followed by further treatments with ammonium ion and/or rare earth metal ions, and a metal passivating agent [52].

The performance of ChemCat–Coastal process was examined at Coastal eagle point FCC unit, 53,000 b/day Kellogg model 3 [13]. The spent catalyst was processed and recycled at the rate of 10 t/day, and the results are shown in Table 4.

Magnesium oxide containing 25% SiO_2 can adsorb most of the metals, Ni, V, Cu, Fe, etc. present in the FCC feedstocks to maintain the cracking activity [53]. Magnesium oxide and magnesium aluminate spinel [54], oxides of Al, Mg and Ca [55], and sponge coke particles [56] are also reported to be effective for removing metals, in particular, vanadium.

Table 3
Catalytic activity of virgin, metal-contaminated and demetalated catalyst

	Metal content (%)			Catalytic activity		
	Ni	Fe	V	MA	CPF	H_2/CH_4
Virgin catalyst				80.0	0.75	8.0
Metal contaminated equilibrium catalyst	0.29	0.78	0.73	59.1	3.02	20.0
Process	Metal removal %					
Demet III	86	50	42	69.9	1.06	6.20
	86	55	48	70.5	1.20	7.65
Demet IV	0	3	47	70.9	1.52	8.70
	3	0	51	71.8	1.22	8.89
	4	0	59	72.9	1.28	7.14

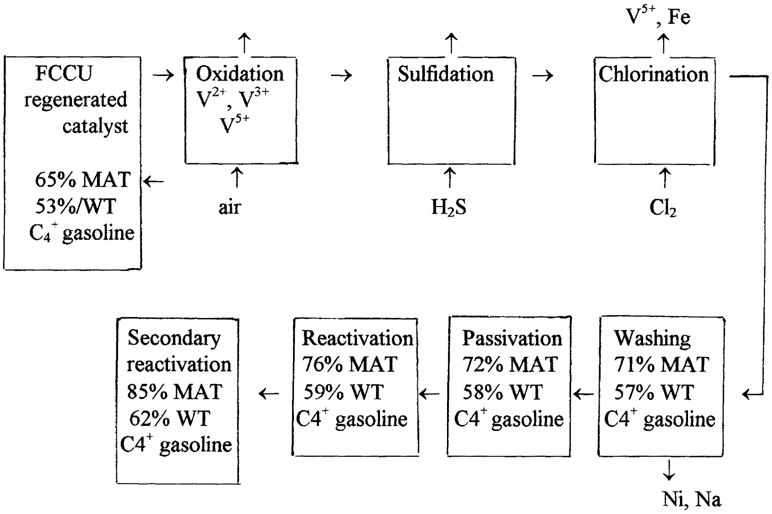


Fig. 9. Schematic flow diagram of ChemCat/Coastal's Demet process.

Table 4
Performance of Demet process at Coastal Eagle Point FCC unit

	Pre-Demet (t/day)	Demet applied (t/day)
Fresh catalyst	15	8.5
Catalyst loss	3	1.5
Withdrawal	12	7.0

3. RFCC catalysts

The principle chemistry of the RFCC process is the same as that of the FCC process except that the resid oil is used instead of the gas oil feed. The RFCC should perform more functions to deal with impurities in the resid oil. Kellogg, S and W, IFP, UOP and Shell have developed their own RFCC processes by introducing new technologies. More than twenty RFCC units have been built worldwide in recent years. In the US using 50% of the world FCC–RFCC catalyst, about half of them was discarded in the past. As stated above, reutilization of the spent catalyst becomes a main concern worldwide now.

Nickel and V sulfides are deposited on the catalyst during the resid hydroprocessing. These metal sulfides eventually plug the catalyst pore structure, deactivate the catalyst and the resulting deactivated catalyst must be replaced for sustaining the operation of the RFCC unit [57]. For example, 3000 pounds of V/day were picked up at 90% metal removal rate in a 50,000 b/day unit processing a resid with 200 ppm V. If the catalyst were replaced after picking up 10% of the weight of V, the catalyst usage would amount to 30,000 pounds/day. Several such resid units were on stream in the early 1980s [58]. Thus, large quantities of spent catalyst needed to be disposed in an environmentally acceptable way. In addition to V, the resid catalyst could contain Co, Ni and Mo sulfides and trace amounts of other metals [59]. One potential use for the spent catalysts is as a source of metals, in particular V [60]. Thus, vanadium must be separated from the other catalyst components in the final step.

In the usual commercial separation scheme (Fig. 10), vanadate and molybdate ions were extracted from the catalyst by leaching with alkali [61]. Prior to the leaching step, the catalyst was usually oxidized to convert metal sulfides to oxides and to raise Mo and V to their highest oxidation states. Sodium vanadate and molybdate were recovered as an alkaline solution and were separated by fractional precipitation.

An improved method for separating V and Mo was revealed by extraction of vanadate with a quaternary ammonium salt, tricaprylylmethylammonium chloride, from the aqueous alkali leaching solution of molybdate and vanadate [62]. Separation of Mo and V from each other was carried out with a synthetic mixture containing 3.45 g $NaVO_3$ and 1.92 g

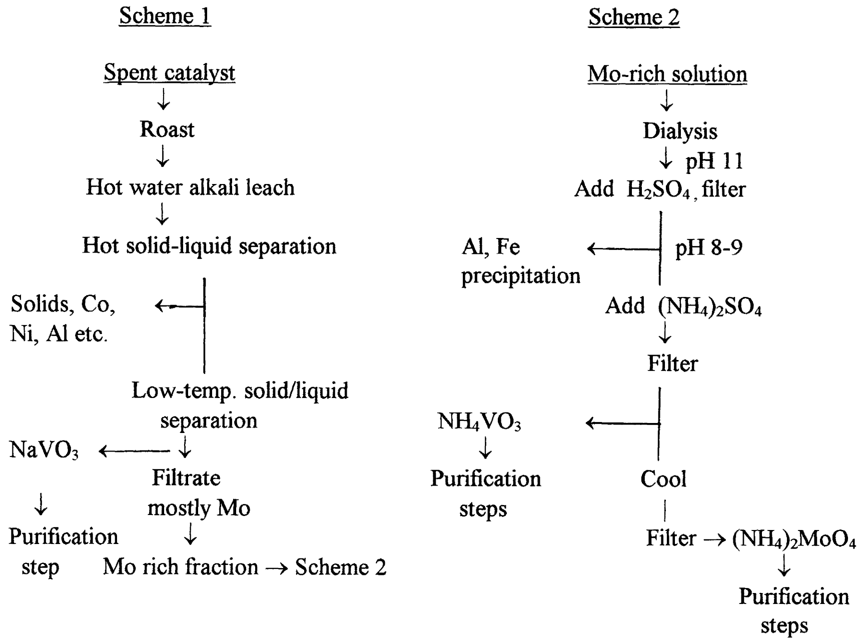


Fig. 10. Metal removal schemes for RFCC catalyst.

Na_2MoO_4 in 50 ml water by the two-stage extraction [63]. Details of the procedure are shown in Fig. 11.

A substantial improvement in the catalytic activity of $NiO–CoO–MoO_3/Al_2O_3$ and spent FCC catalysts was achieved by using a dilute aqueous solution of a complexing agent such as oxalic acid, lactic acid, citric acid, dioxane, acetylacetone [64]. Regeneration of hydrogenation catalysts used for H–oil and H–coal processes was done by dissolving the deposited metals with an aqueous solution of sulfuric acid and ammonium ion [65], and ammonium peroxydisulfate [66].

4. HDS catalysts

Metals such as Co, Mo, Ni, W, and V were recovered by leaching the spent HDS catalyst roasted in air at 400–600°C with an aqueous solution containing NH_4OH, $(NH_4)_2CO_3$, $(NH_4)_2SO_4$ and H_2O_2 at 50–95°C [67], 9 wt% of H_2O_2 solution stabilized with L(+)-ascobic acid [68], an aqueous H_2O_2 solution stabilized with oxalic acid [69], NaOH and $Na_2Al_2O_4$ [70,71], oxalic acid [72], W as $CaWO_4$, Na_2WO_4, and $(NH_4)_2O_{12}WO_3.5H_2O$, and an aqueous solution of $NH_4OH–(NH_4)_2CO_3$ at pH 9.5–11 [73].

	Second-stage extraction
Feed:	3.45 g (0.028 mol) $NaVO_3$ and 1.92 g (0.009 mol) Na_2MoO_4 in 50 ml water
First stage:	Extract with 100 ml of tricaprylylmethylammonium chloride in xylene
Second stage:	Extract the first-stage extract with 50 ml water
	Extract the first-stage raffinate with 100 ml, 20 wt% tricaprylyl-methyl–ammonium chloride in xylene

The V- and Mo-oxy anions in the resulting leached solution were extracted with a quaternary ammonoium compound in the presence of $C_{10}H_{21}OH$ [73].

Roasting the calcined catalyst with NaCl in N_2 at 850°C for 2 h, subsequent leaching of the resulting catalyst with boiling water for 1 h dissolved 81.85% V, 81.78% Mo and minor portion of other components. Separation of V from the leaching solution was carried out efficiently by precipitating NH_4VO_3 via liquid–liquid extraction using bis(2-ethylhexylphosphate) and tri-*n*-octylamine and subsequently stripping and

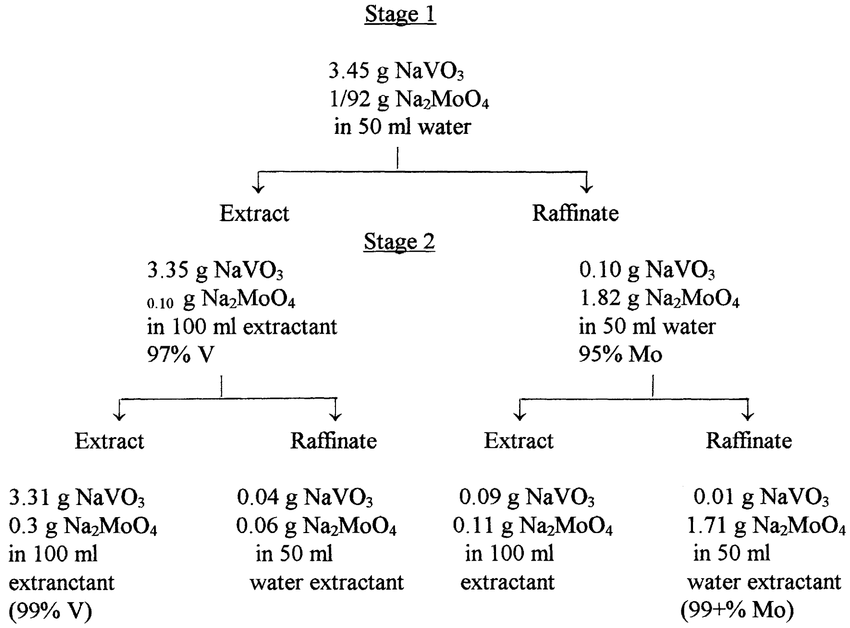


Fig. 11. Two-stage extraction of V and Mo from the synthetic feed of $NaVO_3$ and Na_2MoO_4.

precipitation. The overall recoveries of V and Mo were 75.5 and 77%, respectively [74]. The spent catalyst was mixed with 10% Na_2CO_3, 20% coke, and 5% clay, and fired at 1100°C for 30 min, and extracted with H_2SO_4 to recover 80.9% Mo, 85.7% Co, and 86.3% Ni [75].

The presulfided catalyst was extracted with 0.4 wt% (pH 2.3) heteropoly acid such as molybdophosphoric acid with 15% H_2O_2 [76,77], and isopropyl alcohol or ethylene glycol to selectively remove vanadium [78]. An aqueous solution of EDTA with pH between 7 and 11 selectively removed V from other catalytic components such as Co and Mo [79]. Both presulfided HDS and FCC spent catalyst were treated with a solution containing Fe^{3+} and/or oxidizing bacteria to recover metals as metal ions [80].

Ammonium citrate leaching [81], oxalic acid extraction study of V_2S_3 and NiS as model compounds of spent atmospheric HDS catalyst [82–84], and 1–2 wt% of hydrazine sulfate solution leaching method [85] have been reported as an effective extraction procedure. Addition of 6% H_2O_2 as an oxidizing agent to Na_2CO_3 extraction solution increased extraction of Mo and Ni from the HDS catalyst, from 48% to 98% and from 49% to 85%, respectively [86].

5. Spent catalysts from other various processes

The catalysts used in the hydrotreating processes deactivate rapidly as a result of depositing coke and metals on the active catalyst surface [82,87,88]. The metal contaminants such as vanadium are usually concentrated near the outer surface of the catalyst pellet, blocking pore mouths and reducing the active surface available within the inner pores of the catalysts [89–91].

Several methods have been reported in the literature for the leaching of metal contaminants from spent heavy oil hydrotreating catalysts [83,92,93]. Organic and inorganic acids have been used as a reagent for metal leaching from spent catalysts [93–95]. Various organic acids have been used for rejuvenation of spent residual oil hydrotreating catalysts. The efficiencies of different organic acids for selective leaching of metal contaminants from coked and decoked forms of spent catalysts have been defined [96,97] The effect of adding an oxidizing agent such as H_2O_2 or ferric nitrate to the organic acids, e.g., oxalic acid on the leaching efficiency, and the metal leaching kinetics and mechanism are thoroughly examined [85,98,99]. Considering both kinetics and mass transfer aspects that the metal leaching initially involves extraction of deposited metals from the pore mouths until pore structure develops followed by the removal of metals from the structure, a model for metal contaminant leaching from spent catalysts has been developed [100].

A mixture of mono-octylbutylphosphonate and Disersol (16:84) was contacted with an aqueous solution (pH 6) containing Ni, Co and $(NH_4)_2SO_4$ at the organic–aqueous phase ratio=1. The Co–Ni separation coefficient (metals concentration ratio in organic vs. aqueous phase) was 27,140 [101]. Vanadium was also recovered from the spent catalyst, ore and industrial wastes by extracting it in the presence of V(+2) ions, the resulting sludge was separated and used to prepare new catalysts. The resulting V(+4) was oxidized to V(+5), which was again extracted with aliphatic amines, treated with H_2SO_4, and back extracted in the presence of ammonium persulfate to produce $(NH_4)_3VO_4$ [102]. A combination of HCl and subsequent NaOH leaching procedure gave a good V recovery (94%) from oil-fired boiler slag [103].

After an effluent from the HDS process containing Mo, V, Ni and Co was adjusted its pH below 3, it was extracted with amine (primary, tertiary) and quaternary ammonium salt to extract Mo and V into the organic phase, and Co and Ni in an aqueous phase. The resulting organic phase was again treated with aqueous alkaline solution to extract Mo and V [104]. Mixed solution of $(NH_4)_2CO_3$ and H_2O_2 was proven to be an effective extracting agent for the spent desulfurization catalyst system. The pretreatment procedure such as removal of sulfur and coke, and the oxidative calcination were not required [105].

Approximately, 95% of V was extracted from electrostatic precipitator ashes of the oil power plants with 0.1–0.2 M H_2SO_3 which was prepared by dissolving SO_2 gas in distilled water, at 50–90°C (Table 5) [106]. Ashes usually contains a large amount of ammonium bisulfate.

Table 5
V removals from electrostatic precipitator ashes of an oil power plant by various reducing agents

Agent	Extracted % of metal			
	Mg	Fe	Ni	V
Distilled water	83	18	60	1.4
0.1 M H_2SO_4	88	53	61	20
0.1 M H_2SO_3	89	59	68	94
$(COOH)_2$	89	59	69	97
HCHO	91	42	57	17
HCOOH	68	54	50	35

Among other reducing agents, oxalic acid was as effective as H_2SO_3, whereas both HCHO and HCOOH was much less effective. Vanadium was recovered as V(+5) from spent Ni–V hydrogenation catalyst by extracting with acid and oxidizing the resulting extract in a two-step process [107]. In the first step, V(+4) was obtained by oxidizing with an O_2-containing gas at pH 1.5–2.4. In the second step, further oxidation was carried out at 70–110°C and pH 2.6–4.0 to precipitate V(+5) compounds in a form of $V_2O_4{\cdot}6V_2O_5{\cdot}nH_2O$. The filtrate contained a small amount of V. Metals such as Mo, W, Ti, V, Ta, and Nb were recovered from the reaction effluents produced in the process of epoxidizing alkenes with hydroperoxides, by adding ~10% water, heating in an autoclave under pressure at 200°C for 4 h. 98.7% of Mo was recovered [108]. Vanadium and silica were recovered from the spent catalyst from the sulfuric acid plant by leaching with NaCl and NH_4OH solution. Also vanadium was obtained from the filtered solution by precipitation with HNO_3, while the leached residue was reacted with NaOH for SiO_2 recovery [109].

The spent Mo–Co–Bi–Ni–Fe catalyst on SiO_2 from acrylonitrile manufacturing was extracted with an aqueous solution of NH_3 and NH_3/CO_2 ratio=(2–5):1 at 20–80°C to recover Mo, Ni and Co [110]. The residue was dissolved in HNO_3 at 90–110°C to solubilize Bi and Fe, and then Co, Ni, Mo, and Bi were individually recovered by the conventional methods. Another spent ammonia oxidation catalyst from the HNO_3 plant was mixed with Na_2CO_3 at 950°C, and the mixture was melted and leached with water at 50–90°C for 1 h. The Co_3O_4 filter cake was obtained [111].

6. Precious metal recovery

Recovery of precious metals has been an important topic not only for the economic aspect but also for recycling rare natural resources. Recently many technologies have been suggested, and some of them are being practiced for the commercial applications. It is impossible to cover many technologies reported in the area, and thus, author focused mainly in two areas such as the spent automobile catalyst and various types of catalysts generated from many sources such as petroleum refining, petrochemicals, commodity and fine chemicals, in particular, pharmaceutical processes.

6.1. Auto catalyst

The recovery technologies of precious metals such as Pt, Pd, and Rh from the spent automotive catalyst in the catalytic converters were thoroughly reviewed [112,113]. There are two segments in the recovery technology, i.e., the pretreatment procedure, and the refining step for obtaining highly pure metals. Two types of methods, namely, wet and dry processes, have been commercially practiced. In the wet process, precious metals on the spent catalyst were dissolved mostly in the form of chloro-complex, MCl_6^{2-}, by contacting with an aqueous solution of chlorate, perchloric acid, Cl_2, H_2O_2, bromate, nitrate, and aqua regia [113].

$$3Pt + 4HNO_3 + 18HCl = 3H_2PtCl_6 + 4NO + 8H_2O$$

The resulting solution, in which precious metals are present in a low concentration, are further treated to concentrate them, and subsequently metal ions are reduced to 0 oxidation state by introducing metal such as Al, Fe, and Zn. in a concentrated system. In short, precious metals can be recovered as highly pure metal from the extracted solution via the reductive separation process. Reducing agents such as hydrazine have also been known to be effective for the reaction.

$$H_2PtCl_6 + 2Al = Pt + 2AlCl_3 + H_2$$

In the dry process, the catalyst supporting matrices such as alumina, mullite, and cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2$) are melted, in some case with CaO, at elevated temperatures to obtain a low viscous slag. Precious metals in the melt are separated by allowing them to adsorb on Fe or Cu having high specific gravity. Other methods using the ion exchange resins, chelating agents, and direct solvent extraction processes will be discussed in later section.

Other processes, which cannot be classified as the conventional wet and dry process described above, include the carbonyl vaporzation method, chlorination, and segregation process. In carbonyl vaporization method, volatile precious metal carbonyl chlorides are formed by reacting with CO and Cl_2.

$$Pt + Cl_2 + CO = Pt(CO)Cl_2$$
$$Pd + Cl_2 + CO = Pd(CO)Cl_2$$

In chlorination method, precious metals on the auto catalyst are chlorinated with Cl_2 at an elevated temperature [26,114–116]. It requires temperatures higher than 1200°C to vaporize these metals. But an addition of NaCl becomes necessary for Rh since anhydrous $RhCl_3$ is insoluble in acid. The best properties of these two processes are combined to make the segregation method [117]. The metallurgical approach is a recently developed process called Rose process, in which Cu-containing precious metals is treated in the oxidizing atmosphere, and CuO is separated from precious metals [113]. In general, the fundamental chemistry involved in the segregation process can be described as follows:

$$CaCl_2 + SiO_2 + H_2O = CaSiO_3 + 2HCl$$
$$M_xO_y + HCl = MCl_n(gas) + H_2O$$
$$C + H_2O = H_2 + CO$$
$$M_xO_y(gas) + H_2 + CO + 1/2O_2 = M + H_2O + CO_2$$

The methods discussed above have known to be not effective for the metal–honeycomb- and ceramic–honeycomb-type auto catalysts. Since the catalyst layer has a strong bond with the supporting matrix, neither thermal shock nor alkali leaching is sufficient to separate the precious metal catalyst component from the supporting matrix.

Commercial processes for precious metal recovery from auto catalysts are summarized in Table 6. Details of the process along with the process flow schemes are fully discussed in a previously cited reference [113].

The process flow diagrams of the aqua regia process and chlorination method are selected as a representative case for the wet and dry process, respectively, in Figs. 12 and 13. Also, the process diagrams of Rose process and segregation method are shown in Figs. 14 and 15, respectively [113].

The Pt, Pd, and Rh on porous inorganic carriers are treated in a closed vessel with an inorganic acid and an oxidizing agent by increasing the concentration of the

Table 6
Main precious metal recovery processes from auto catalysts

No.	Process	Specification	
1	CN extraction	Wet	US Bureau of Mining
2	Aqua regia	Wet	
3	Chlorination		Tanaka Kikinzoku
4	Segregation		N.E. ChemCat
5	Melting method-1	Dry	
6	Rose method	Dry	Nippon P.G.M[a]

[a] Nippon Precious Group Metal.

acid to dissolve these metals for their recovery [118]. The Pt and Pd loaded on granular or honeycomb Al_2O_3, SiO_2 or carbon support were leached with aqua regia and filtered. The resulting filtrate (pH 1.0) was stirred with Fe powder, and filtered. The residual Fe powder was separated magnetically and recycled. Recoveries of Pt and Pd were 95.0% and 92.7%, respectively [119]. The spent catalyst containing 1000 ppm Pt, 200 ppm Pd and 300 ppm Rh on Al_2O_3 was heated in aqua regia for 5 h, filtered, and the residue was washed with water acidified to pH 1 with HCl. The recoveries of Pt, Pd, and Rh were 99.0, 100, and 86.7%, respectively [120].

6.2. *Precious metal-containing catalysts from various processes*

Precious metals on the bimetallic reforming catalysts, $Pt/Re/Al_2O_3$, $Pt/Ir/Al_2O_3$, its iron-doped counterparts, $Fe/Pt/Re/Al_2O_3$ and $Fe/Pt/Ir/Al_2O_3$, and single metal catalyst, Pt/Al_2O_3, were recovered by dissolving them with an oxalic acid solution buffered at pH ≥ 3 with ammonium oxalate [121]. The spent $Pt/Re/Al_2O_3$ catalyst was calcined and mixed with hot H_2SO_4 to dissolve Re and most of Al_2O_3, filter to separate Pt and undissolved Al_2O_3, the filtrate was passed through a strongly basic anion exchange resin, then Re was eluted by a mixture of 1–8 N $HClO_4$ and 1–25% EtOH, EtOH was evaporated off for recycle, and the resulting solution containing $HReO_4$ and $HClO_4$ was sulfided with H_2S to harvest Re as Re_2S_7 [122].

The Precious metals such as Pt, Pd, and Rh were recovered from the precious metal containing Fe alloy by leaching with chloride solution mixed with a small amount of HNO_3, reducing them with powdered Fe metal, dissolving the resulting precious metals with HCl and an oxidizing agent selected from Cl_2, H_2O_2, O_2 and air, extracting Pd with a series of organic extracting agents such as dihexylsulfide for recovery of Pd, extracting with a carboxylic acid series solvent for the removal of impurities from the aqueous phase, and extracting Pt and Rh with tributylphosphate for their recovery [123].

Palladium was recoved from still heels by treatment with HCl and conversion of Pd to crotylpalladium chloride which was used as the catalyst in the carbonylation of chlorobutenes to form 3-pentenoyl chloride [124]. It was also recovered from waste aqueous solutions from manufacture of Sulbactam antibiotic over a Pd/coal catalyst. The waste solution-containing soluble Pd (pH 8–13) was treated with Na dithionate at

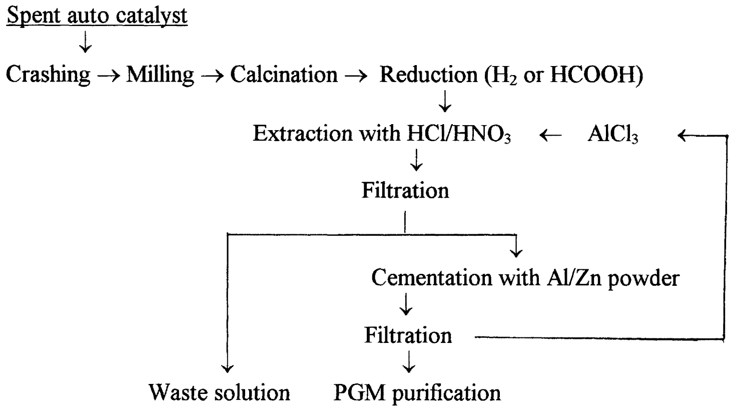


Fig. 12. Process flow of aqua regia method.

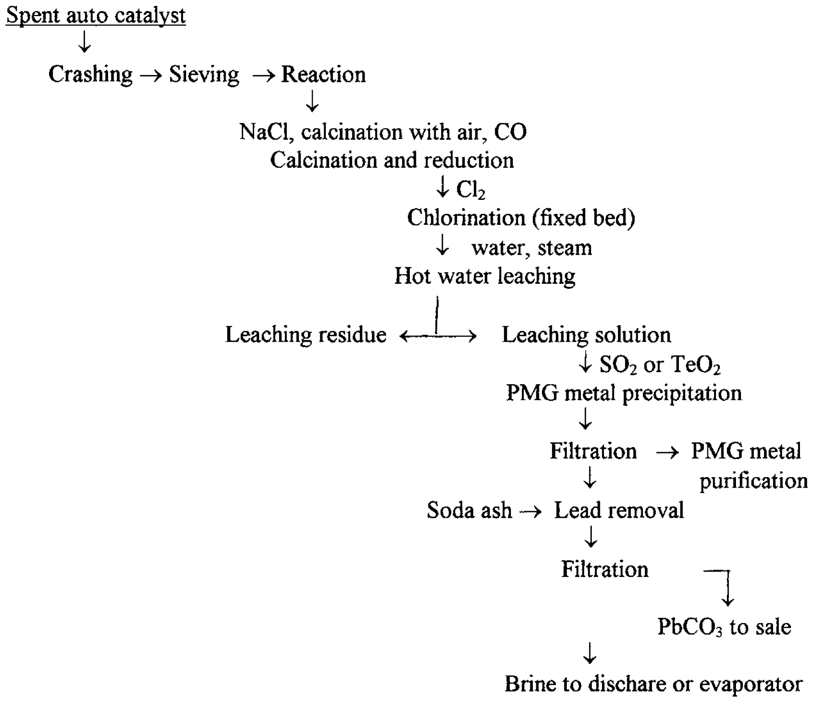


Fig. 13. Process flow diagram of chlorination method.

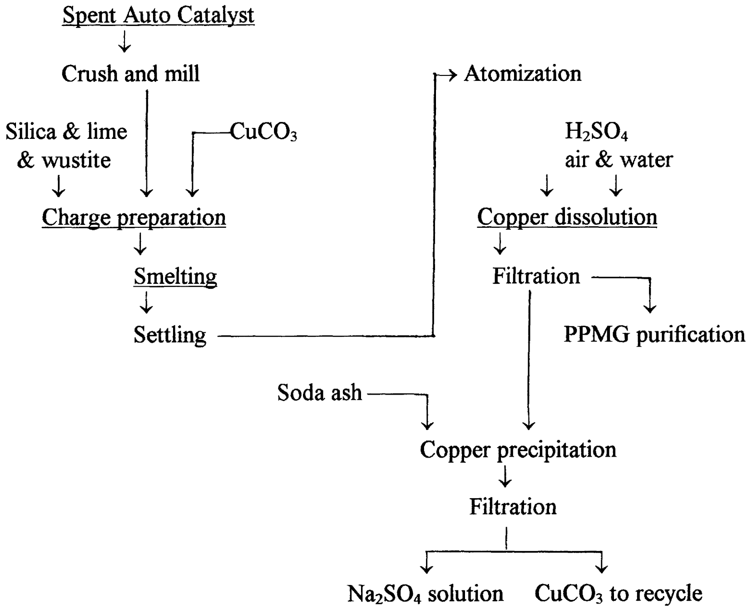


Fig. 14. Process flow diagram of the Rose process.

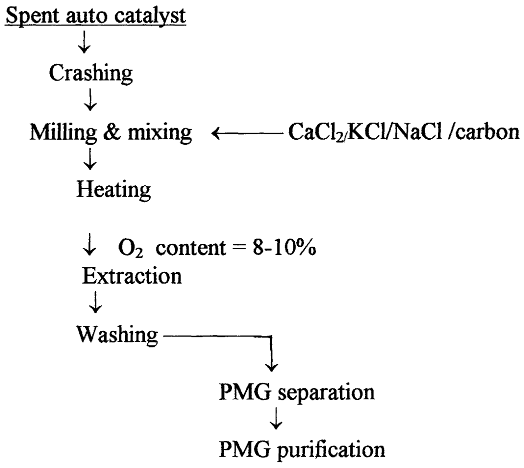


Fig. 15. The process diagram of the segregation method.

Na dithionate/Pd wt% ratio of 2–30:1 and 60–120°C. After cooling, precipitated Pd was separated [125]. Palladium present in an organic solution resulting from the catalytic reactions was extracted with water–base solution. The water–base solution was neutralized, and then Pd was extracted with an organic solvent. The tramp metals remain in the water phase [126].

A liquid containing Pd(II) salt resulting from oxidative coupling of an aromatic compound was heated at 180–280°C, and stirred under H_2 to precipitate Pd particles in the presence of Cu powder. The liquid containing Pd acetate and Cu acetate catalyst for dimerization of dimethylphthalate was autoclaved for 4 h at 220°C, and 500 rpm stirring under 30 kg H_2/cm^2 to reduce the metal acetates with *o*-phenanthroline. Colloidal particles of Pd black and powdered Cu were obtained [127]. Pd was recovered in excess of 98% from Pd/C catalyst scrap by oxidative roasting and leaching in HCl [128], and it was also electrodeposited on Pt anode from a suspension of roasted catalyst in diluted HCl. The electrodeposited Pd was electrochemically dissolved, and recovered as $PdCl_2$ solution [129].

The Pt recovery was increased from the gauze-type screen manufactured with Pd (5%)–Co alloy fibers used for the NH_3 oxidation process and reduction of N_2O emission [130], and it was also recovered from the waste stream produced from the HNO_3 production plant by treating with aqua regia and NH_4Cl to precipitate it as $(NH_4)_2PtCl_6$ followed by thermal decomposition at 800–900°C to obtain Pt black [131]. The Pt dust (67%) was again recovered from the HNO_3 manufacturing plant via oxidation of NH_3 by catching with fine meshes made of Ce (0.2%)–Pd fibers and fine meshes made of stainless steel fibers [132]. Pt and Ce were recovered from the spent catalyst by heating in a reducing atmosphere to convert Ce to its trivalent compound, and extracting with HCl at 60°C [133].

The spent catalyst sieve containing Pt and Rh was dissolved in aqua regia, and the concentrated solution was converted to chlorides with HCl, treated with aqueous saturated NaCl solution, adjusted pH to be 1–1.4, and contacted with an acidic cation exchanger to separate common elements. Residual solution after the ion exchange was treated with aqueous 25% NH_4OH to pH 9 to obtain NH_4–salts of hexachlorocomplexes. The salts were reduced with hydrazine hydrate. After filtration, the resulting Pt–Rh powder was washed with water and dried at 110°C. Typical yield of the high-purity product was 99.8% [134].

The spent Pt–C catalyst from manufacturing of hydroxylamine sulfate was irradiated by using 2500 W IR heater. The resulting ash was dissolved by using excess aqua regia for 1 h at 80°C to give Pt in 100% yield, and the recovered Pt was used to prepare the Pt–C catalyst for reuse [135]. Carbon tetrachloride vapor in flowing air or N_2 was used for the extraction of Pt from a spent catalyst of naphtha reformates. More than 95% of Pt was recovered [136].

The Pd (1%) or Pt (1%) on Al_2O_3 pellets were mixed with C and heated under a flow of Cl-containing gas such as $CoCl_2$, CCl_4, $SOCl_2$ and S_2Cl_2 at 800–1000°C for 8 h to convert the metal oxides into chlorides for evaporation. The Al_2O_3 support was converted into $AlCl_3$, and the residual solids were then separated by gravity concentration to recover both Pd and Pt in 99% yield [137,138]. In general, efficient precious group metal (PGM) recovery was achieved by washing the flocculated filter cake [139].

7. Regeneration by physical methods

The equilibrium FCC catalyst was regenerated by alternate exposure to oxidizing and reducing atmospheres for reuse [140]. Among various physical methods, both magnetic separation and density grad-

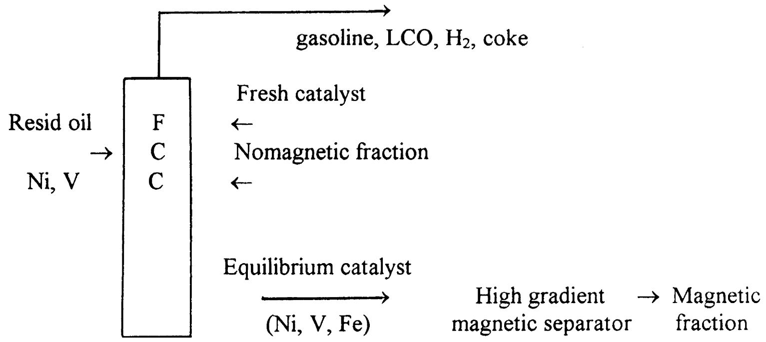


Fig. 16. Schematic flow diagram of magnetic separation of FCC.

ing have been mainly used in the commercial operations.

7.1. *Magnetic separation of FCC equilibrium catalysts*

The equilibrium FCC catalyst was separated by the high-gradient magnetic separator [141,142], and magneto hydrostatic separator [143]. The particles made magnetic by the deposition of Ni, V, Fe, and Cu were separated from non-magnetic particles and returned to the reactor for recycle. An FCC equilibrium catalyst was subjected to the high magnetic separation by the scheme shown in Fig. 16, and the concentration of Ni on the magnetic fraction was shown in Fig. 17 [51].

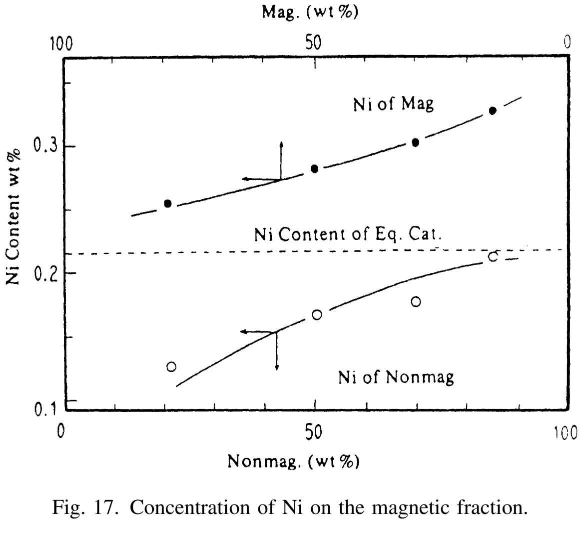


Fig. 17. Concentration of Ni on the magnetic fraction.

The commercial test of the above separation process was carried out in the RFCC unit (3700 barrel/day) attached with the high gradient magnetic separator, Yokohama refinery, Nippon Petroleum Refining. The operation of the magnetic separator as well as the FCC unit were smooth without any trouble during the 2-year testing period. The result of this test proved the validity of the magnetic separation process concept and approximately 25% of the catalyst saving was realized with this process by comparing the amount of the fresh FCC catalyst required to maintain a certain level of Ni on the equilibrium catalyst in the FCC unit with and without the magnetic separation [51].

The precious metal containing spent catalyst supported on Al_2O_3 or cordierite was melted with CaO and coke in an inert atmosphere to form a self-collapseable slag and concentration of precious metals from the resulting powdered slag was carried out by magnetic separation [144]. The waste catalyst containing Pt and Rh was pulverized, and separated from the waste catalyst via magnetic separation in water or an aqueous solution of chemicals under supersonic vibration [145].

7.2. *Density grading*

The apparent density of the catalyst particles increases as the amount of the metal deposited on the catalyst increases under the petroleum processing conditions, and the catalytic activity decreases, correspondingly. The regenerated resid hydrodesulfurization (HDS) catalyst, Co–Mo–Al_2O_3, the cylindrical radius 1/16 in (1.6 mm), was graded into three fractions based on the apparent density difference among

Table 7
Density grading of regenerated resid catalyst containing heavy metals

Catalyst	Yield (vol%)	S.A. (m^2/g)	Ni (wt%)	V (wt%)
Fresh	–	200	0	0
Spent catalyst composite	–	1.53	0.16	1.7
Light	19	1.66	0.05	0.5
Medium	53	161	0.1	1.4
Heavy	28	114	0.47	4.8

the catalyst particles, and the results are shown in Table 7 [146]. In general, the deactivated catalyst is regenerated by burning off the coke, and the optimum regeneration temperatures for Co–Mo, Ni–Mo, Ni–W, and zeolite catalyst are 460–500, 430–470, 480–520, and 400–430°C, respectively. The metal content (1.9% Ni+V) in the catalyst composite was concentrated to the heavy fraction (28%) containing 5.27% Ni+V by this technique. The metal contents for the light and medium fractions are 0.55 and 1.53%, respectively, and these two fractions (72%) maintain surface area higher than 80% of that of the original catalyst composite, and thus can be recycled. The heavy fraction can be used for the metal recovery and rejuvenation.

8. Conclusions

The catalyst wastes have rapidly been increasing worldwide due to an increase in newly constructed RFCC units and the advent of new processes using various novel catalysts. Regeneration and recycling of the spent catalysts became an unavoidable task not only for lowering the catalyst cost but also for reducing the catalyst waste to prevent the environmental pollution. Although one should strive to achieve a total recycle of the catalytic material, there may exist some of catalyst waste materials that cannot be regenerated and recycled within a reasonable economic burden based on the currently available technology. Thus, it is essential to make continuing efforts to develop new cost effective catalysts which can be regenerated and recycled for the catalyst users as well as producers. Furthermore, the catalyst manufacturers ought to consider an inescapable fact that the future catalyst must be unusually stable to provide the long catalytic life and should be readily regenerable and/or recyclable to be a commercially viable system. These underlying environmental concerns must be reflected on designing a new catalyst from the very beginning stage of the catalyst development. In other words, the recovery of metals, rejuvenation and/recycling of the spent catalyst ought to be incorporated as a part of the total strategy of the business using the catalytic reactions.

Various methods for recovering precious metals from the spent auto catalyst, petroleum reforming and other industrial catalysts are reviewed with the dual objectives of renewing the valuable resources and preventing the catalyst waste production. The processes using aqua regia, promoted chlorination, segregation method and the Rose process are among them.

Several generations of Demet processes are fully described for the regeneration of spent FCC and RFCC catalyst. These technologies can also be directly applicable to remove metal components from the toxic waste materials containing high levels of metals to convert them to the innocuous materials for the safe landfill and/or raw materials to make the secondary useful products. Currently, the catalyst manufacturing firms, petroleum companies, and many environmentally oriented engineering companies are actively engaged in R and D work to come up with more effective catalysts, which can meet these objectives. It is expected to have a breakthrough to improve the catalyst function, in particular, catalyst stability and life, and its operating process, which can comply with the environmental regulations with a reasonable cost.

Appendix A

The microactivity test (MAT): In the standard microactivity test developed by Atlantic Richfield, the catalyst to be tested is pelleted from its powder form by a single punch machine. The pellet is 1/32 in in diameter and 1/8 in long and has 0.5–1 kg of crushing strength. It is calcined in air at 482°C for 3 h before it is used. One ml of the standard feedstock oil is charged automatically over 5 g of pelleted catalyst packed in a reactor made of two concentric glass tubes of 10 mm i.d. at 482°C. The cracking reaction is performed for 5 min to determine the activity of the catalyst. The activity of the catalyst is defined by volume percent conversion of 221°C (430°F) plus material in the feed to 221°C minus product.

The liquid product is continuously collected in a calibrated microreceiver while the total gaseous product including the purge nitrogen is collected over water. This product is then injected into the GC unit to determine the liquid yield. The spent catalyst is removed from the reactor for determination of carbon content, which then provides the basis for calculating a carbon-producing factor (CPF). The gaseous product, which is sampled in an evacuated gas bomb, is analyzed for hydrogen and hydrocarbons and is used to determine the molar ratio of hydrogen to methane. The ratio is an indication of the gas making function of the catalyst at the expense of the liquid products, gasoline. It was usually obtained at 95–96% material balance in this test.

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