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Review

Spent refinery catalysts: environment, safety and utilization

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1. Introduction

The distillation of crude oil is an essential step in the petroleum refining practice. The yield and properties of produced distillates depend on the properties of crude oil, distillation conditions and the type of distillation column. Primary distillates are subjected to an additional treatment to meet the environmental requirements and the performance of produced fuels. The schematics of a typical refinery operation processing a conventional crude shown in Fig. 1 [1] lists four catalytic processes, i.e. reforming, hydrocracking, hydrotreating, catalytic cracking and alkylation. The residue from atmospheric distillation may be subjected to additional distillation under a vacuum to obtain valuable lubricant fractions which also require catalytic hydrotreatment. Non-conventional refineries can process heavy oils and distillation residues. In this case, the catalytic hydrocracking of the heavy feed is usually the first step, followed by hydrotreating of the synthetic distillates. For the purpose of this review, the hydroprocessing will refer to both hydrocracking and hydrotreating. Light hydrocarbons which are byproducts of several refinery units can be converted to high octane fractions by catalytic alkylation and polymerization. Thus, several operations employing a catalyst may be part of the petroleum refinery. The management of catalyst inventory represents an important part of the overall refinery cost. As shown in Fig. 2, the development of refining is closely connected with the growth of the use of catalysts [2]. In the past, refining catalysts accounted for more than half of the total worldwide catalyst consumption. Today, because of the importance of environmental catalysis, refining catalysts account for about one third of the total catalyst consumption. Future advances in development of more active and stable catalysts may further decrease the overall consumption of refinery catalysts.

Two principal groups of refinery catalysts include the solid and liquid acids catalysts. The HF and H_2SO_4 used in alkylation processes are the most widely used acid catalysts. The solid catalysts are usually of a non-noble and noble types. Non-noble metal catalysts include base metals and zeolites. Noble metals include a variety of precious metals from the platinum group. In many cases, catalytically active metals are combined with a solid support such as alumina, silica, silica–alumina, zeolites, carbon, etc. Catalyst development is a very active research area. New types of catalysts are being developed to meet challenges which the refiners will have to face in the future. In this regard, the development of solid alkylation catalysts is perhaps the most active area of research.

The marketing study published by the Freedonia Group Inc. [3] provides interesting infor-

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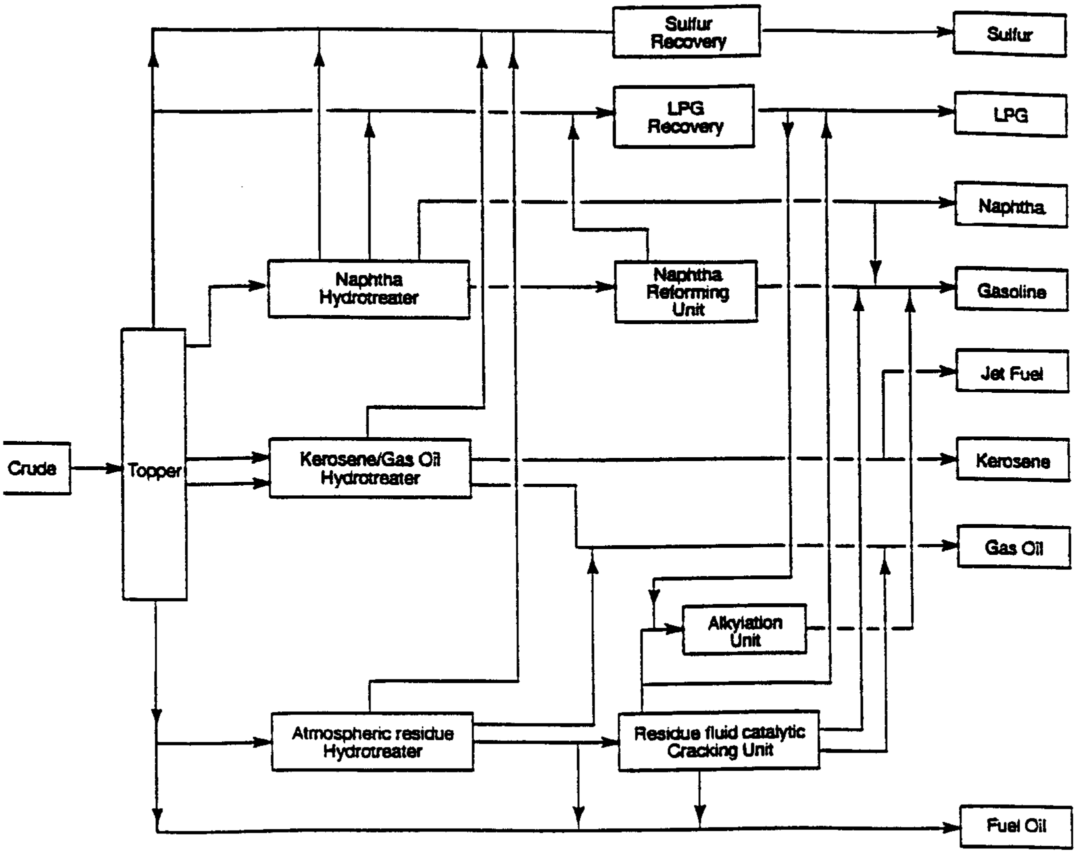

Fig. 1. Flowsheet of petroleum refinery [1].

mation on the consumption of refinery catalysts in the US on a volume basis. As the results of this study (Table 1) show, acids used for catalytic alkylation account for about 89% of the volume of refinery catalysts, followed by cracking catalysts which account for about 9%. The remaining (about 2%) include hydroprocessing, reforming and others. The situation is significantly different when the consumption is expressed on a dollar basis (Table 2). For example, reforming catalysts account for less than 0.1% of refinery catalysts on the basis of volume, whereas almost 4% on the dollar basis. At present, cracking catalysts account for more than 40% of the cost but they may be surpassed by hydroprocessing catalysts in the future. The pre-

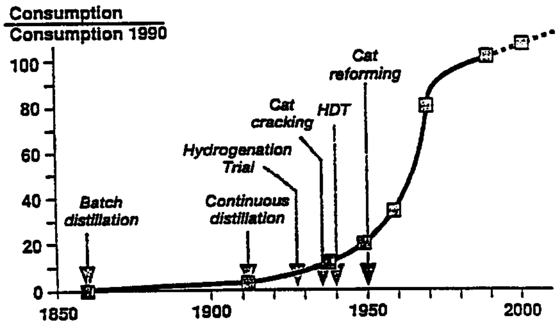

Fig. 2. Oil refining history [2].

Table 1
Refining catalysts demand by volume (lb × 10^6) [3]

	1983	1988	1993	1998	2003
Total demand	4185	4732	5199	5738	6070
Alkylation	3752	4229	4632	5115	5400
Catalytic cracking	387	445	485	510	515
Hydroprocessing	38	44	65	91	128
Reforming	4	5	6	6	6
Others	4	9	11	16	21

Table 2
Refining catalysts demand by value ($\$ \times 10^6$) [3]

	1983	1988	1993	1998	2003
Total demand	504	706	919	1218	1561
Catalytic cracking	248	328	373	440	485
Alkylation	128	178	198	250	290
Hydroprocessing	103	160	293	455	695
Reforming	21	29	39	47	55
Others	4	11	16	26	36

dicted increase of the alkylation catalysts is in line with growing demand for alkylates. The consumption of reforming catalysts is not expected to grow. Thus, a more acceptable approach to improving the quality of the gasoline is to increase the content of high octane alkylates rather than that of high octane aromatics. Other catalysts may also be part of the refinery operation. On the volume and cost basis they usually account only for a fraction of the total catalyst inventory in the refinery. Because of their diverse properties and structures, the other catalysts will be discussed only very briefly in this review.

In every catalytic operation, the activity of the catalyst gradually decreases. This decrease can be offset by changing some operational parameters. However, at a certain point, catalyst replacement is inevitable. The spent catalysts can be regenerated and returned to the operation. The regeneration of spent hydroprocessing, fluid catalytic cracking (FCC) and reforming catalysts has been performed commercially for several decades. These regeneration processes have been extensively reviewed by Furimsky and Massoth [4], Hughes [5] and Fung [6], respectively. All published information suggests that there is a limit on the number of regeneration–utilization cycles. After several cycles, recovery of the catalyst activity is not sufficient to warrant regeneration.

For the purpose of this review the solid spent refinery catalysts will be referred to as non-regenerable catalysts. Thus, spent alkylation catalysts, including their regeneration will be discussed in a broader sense. Assuming that most of the fresh refinery catalysts shown in Table 1 were purchased to replace the non-regenerable refinery catalysts, these volumes may then approach the amount of spent refinery catalysts. Such catalysts have been attracting the attention of environmental authorities in many countries. There are some indications that all spent refinery catalysts will be classified as hazardous materials in the future. At the present time, among solid catalysts such classification was given to spent hydroprocessing catalysts. Therefore, special precautions have to be taken during

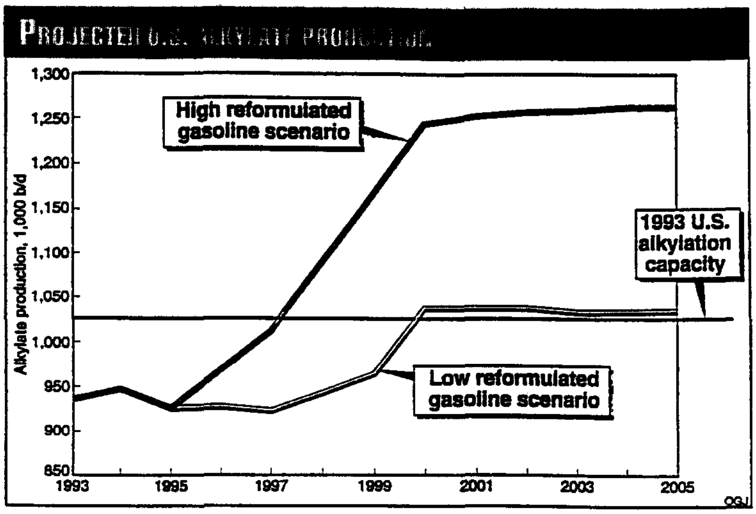

Fig. 3. Projected US consumption of reformulated gasolines [7].

storage, transportation and disposal to avoid future liabilities. The one solution is to find new applications, e.g. cascading, though this may only delay the final decision. But even this may help refiners to buy some time.

Perhaps, the best solution is the reclamation of all components of spent catalysts. The situation is rather straightforward for reforming catalysts because of the high prices of platinum group metals. Thus, in every case the recovery of precious metals is the primary objective. The literature is rich with information on various aspects of metal recovery from spent hydroprocessing catalysts. But this approach is significantly influenced by world prices of base metals which tend to fluctuate.

Alkylation catalysts, such as HF and H_2SO_4 represent a rather unique problem for the refiner because of the toxic and corrosive nature of these acids, in particular that of HF. Nevertheless, at least in a short term, the consumption of the acids is expected to grow because of the gradual replacement of conventional gasoline by reformulated gasoline. An example of trends in the consumption of the gasolines is shown in Fig. 3 [7]. Complex environmental and safety procedures have to be applied during all stages of handling and utilization of these acids, i.e. beginning with their delivery to the refinery and ending with a complete utilization. Because the cost of disposal of the spent acids is prohibitive, all efforts are being made for their reuse. Thus, the regeneration of both spent HF and H_2SO_4 acids becomes an integral part of the refinery operation. The present review will focus on all aspects of management of alkylation catalysts, i.e. environmental and safety aspects as well as on their regeneration and possible utilization.

It is fair to assume that environmental laws will be continuously evolving and some future trends can be anticipated. It is expected that the number of refinery wastes being added to the list of hazardous solids may increase. The development in new analytical techniques will increase the level of confidence in determining the priority species. In this regard, numerous assumptions, speculations and suggestions found in this review are those of the author rather than of any government or organization.

2. Environmental and safety aspects of refinery catalysts

An American Petroleum Institute (API) survey of wastes generated by US refineries, published in 1992, has grouped the refinery wastes into six categories starting with aqueous wastes followed in decreasing order by oily sludges, waste chemicals, contaminated soils, ‘other wastes’ and spent catalysts [8]. About half of the refineries participating in the survey reported progress in the waste reduction due to the modification of processes and procedures, in-process recycling and improved housekeeping. There was some indication of a decline in the landfarming as well.

Today, some refineries are spending between 50 to 90% of cash flow to comply with the environmental regulations [9]. This situation forced many refineries to shutdown the operation. Refineries will be continuously experiencing such pressures from environmental authorities. A competitive advantage may be gained by companies or countries with a low environmental awareness enabling them to produce refined products at much lower costs. It is believed that some global approach is needed to deal with environmental and safety issues in refinery, including spent catalysts, to prevent an unfair competition.

The environmental and safety aspects of refinery catalysts depend on the state of the catalysts. It is obvious that the spent catalysts require most of the attention, followed by regenerated catalysts. Even some fresh catalysts may not be benign and may require some attention. In this regard, of particular importance are acids such as HF and H_2SO_4, which are used as alkylation catalysts. The toxicity of these acids is well known. A separate Section of this review will be devoted to these issues.

Some spent refinery catalysts are already being classified as hazardous wastes. The Environmental Protection Agency (EPA) in the USA defines a hazardous waste as one posing a substantial or potential hazard to human health and the environment if mismanaged. Two basic criteria used to identify hazardous solids include the characteristics which can be defined in terms of physical, chemical or other properties which cause the waste to be hazardous. Also, the properties defining the hazardous characteristic must be measurable by testing protocols and be detectable by generators. The approach the EPA uses to establish hazardous waste characteristics is to determine which properties of the waste would result in a harm to human health or to the environment if the waste is not managed properly. Then, test methods and regulatory levels for each characteristic are determined. Wastes, which exceed the regulatory levels are characterized as hazardous.

The regulations have to be clearly defined to ensure that the hazardous wastes are managed in environmentally acceptable manners. The regulations governing spent refinery catalysts have been continuously evolving. However, many areas such as handling, transportation, storage, etc., are still ambiguous and subject to interpretation. In some cases, the generator, shipper and receiver must seek independent legal or expert advice to determine suitability towards particular situations. The pitfalls which can be encountered during various stages of handling of spent catalysts were described by Rosso [10].

In the USA, the disposal and treatment of spent refinery catalysts is governed by the Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Amendments (HSWA). It is anticipated that the change of these regulations, aimed at decreasing plant emissions, will force some refineries to change the current methods of spent catalyst management. There are at least two regulatory levels in Europe, i.e. one national and the other established by the European Commission (EC). The latter is based on the Basel convention signed in 1989. This regulation establishes three main lists of wastes, i.e. the green list of wastes, which are excluded from the regulations, as well as the amber and red lists to which the regulations apply [11]. However, the question of whether the spent catalysts will be included in either the green or amber and red lists is still under discussion. It appears that the tightening legislation, including the preparation of new directives will supersede the less stringent national legislation, thus constituting the minimum requirements in all EC member states [12]. The latest information suggests that the polluting emission register (PER) developed by the EC is being gradually accepted by the European industry [13]. The PER is based on the US Toxic Release Inventory (TRI). There are some indications of similar activities, with the United Nations (UN) involvement, in countries which are part of the Organization for Economic Cooperation and Development (OECD). In some countries, the refining industry is proactive by actively participating together with the environmental authorities in developing the regulations. This seems to be a better approach than to wait and be surprised at a certain point.

2.1. Classification of spent solid catalysts

According to Raleigh et al. [14], a realistic classification scheme should be based on readily obtainable parameters and not assume that the unlimited physical and chemical characterization data are available. Even if the database is extensive, the inclusion of proper parameters in the scheme and the exclusion of unimportant parameters play a key role in correctly classifying waste solids, such as the spent solid refinery catalysts. On the other hand, some solid wastes may pass through as 'worst case' simply due to the lack of the necessary waste data. These authors have emphasized that an ideal scheme should use documented literature, generator knowledge and professional judgement to rank or classify unknown solid wastes using available waste characterization data.

Nevertheless, a more extensive database may be required to prove that a waste solid is non-hazardous. Thus, in some cases, a hazardous classification may be assigned using rather limited database on the waste solid characteristics.

The essential information for classifying spent refinery catalysts may be found in regulatory documents published by the environmental authorities. An example of the regulations used to determine a hazardous potential of various wastes is the User's Guide to Hazardous Waste Classification, published by the Environment Canada [15]. It is believed that all industrial countries have similar guides. This guide identifies spent catalyst materials among generic types of potentially hazardous wastes. Among the large number of listed activities which may generate potentially hazardous wastes, the energy, with petroleum and coal industries listed as sub-activities, appear to be the most appropriate. The guide gives 16 reasons why these materials are intended for disposal and/or recycling and the same number of the disposal operations. Thus, the spent catalysts can be classified as the substances which no longer perform satisfactorily. Special procedures, which are still evolving, are being applied for disposal of spent catalysts. At least four recycling operation categories listed in the guide, i.e. recovery of metals and metal compounds, regeneration, recovery of components and re-refining and re-use, may be applicable to the spent catalysts.

2.1.1. Potentially hazardous constituents

The guide lists over 50 constituents of potentially hazardous wastes [15]. The constituents which are relevant to spent catalysts are shown in Table 3. One may predict that the number of these constituents will be continuously growing. These constituents can be divided into two groups, such as those present in fresh catalysts and/or are the fresh catalysts (e.g. alkylation catalysts), and those added to the catalyst during the operation. Perhaps, other possibilities are to classify the constituents either as inorganic and organic or combustible and non-combustible. Among spent solid refinery catalysts, hydroprocessing catalysts, especially those from upgrading of heavy feeds, are much more contaminated than the FCC and reforming catalysts because the feedstocks processed in the FCC and reforming operations are either of a conventional origin or were already catalytically treated. However, for spent FCC catalysts, this situation will change once the FCC technology will be widely used for upgrading of the distillation residues.

Table 3
Constituents of potentially hazardous wastes [15]

Compounds of Be, V, hexavalent Cr, Co, Ni, Cu, Zn, As, Se, Te, Ag, Se, Cd, Sn, Sb, Ba, Hg, Pb and Ta.
Inorganic acids
Inorganic sulphides
Inorganic fluorine compounds excluding Ca fluoride
Inorganic cyanides
Phenols
Ethers
Aromatic compounds; polycyclic and heterocyclic
Organic nitrogen compounds; especially aromatic and aliphatic amines
Organic sulphur compounds
Substances of an explosive character
Organohalogen compounds

The Co and Ni compounds which are included in Table 3, are usual components of commercial hydroprocessing catalysts. In this regard, the compounds of Mo and W may also be added to the list in the future. Efforts to develop more active catalysts may require the addition of other metal compounds to the list. The type and amount of constituents which are added during the operation depend mainly on properties of the hydroprocessed feedstock, though the conditions applied during the operation and during the catalyst withdrawal from the reactor after the operation, may also be important. V, Ni, Fe and Ti are the most common metals which are added to the catalyst during the operation. Sb and Sn may be present in spent hydroprocessing catalysts used for hydrotreating liquid products from the FCC operations. Thus, part of the passivators added to

FCC catalysts may end up in the liquid products [16]. Special attention must be given to As and Zn, which can accumulate on the catalyst surface during prolonged hydroprocessing operations, in spite of the fact that their quantities in the feedstock are very small. The information on the other metals which are considered by the EPA to be hazardous pollutants (e.g. Pb, Cd, Hg, Cr, Se, Ba, Ag and Cu) is limited. Significant amounts of alkali and alkali earth metals can also accumulate on the catalyst, especially if the hydroprocessed feedstock was not adequately desalinated. However, these metals will be either combined with the catalyst support or form a crust on the front of the catalyst bed. Sometimes fluorine is added to hydroprocessing catalysts with the aim to prolong their lifetime [17]. The operating conditions applied during hydroprocessing are favourable for the formation of metal sulphides. Therefore, inorganic sulphides will be a predominant form of active metals (Co, Ni, Mo, W and others) and those metals which were deposited on the catalyst during the operation, e.g. Ni, V, Fe and others. The support materials, such as SiO_2, Al_2O_3 and zeolites remain mostly in an oxidic form.

FCC catalysts are usually of a silica–alumina and/or zeolite type. As it was mentioned, Sb and Sn are sometime added as passivators. Additional metals, such as Ni and V may also be present. These metals and passivators may render the spent FCC catalysts hazardous in the future. Two forms of the spent FCC catalysts, i.e. catalyst fines and the usual form of particles deposited by the coke and metals, are being generated. The coke may contain small amounts of sulphur and nitrogen. Compared with hydroprocessing catalysts, the level of contamination of the FCC catalysts with metals and coke is significantly lower because of a much shorter contact time, as well as a less contaminated feedstock. However, continuous efforts to develop new, metals more tolerant FCC catalysts, may result in spent FCC catalysts much more extensively deposited by metals.

In case of hydroprocessing, FCC and reforming catalysts, all organic constituents which are considered to be potentially hazardous (Table 3) are deposited on the catalyst during the operation. N-containing compounds contained in the feed will be adsorbed preferentially because of their basic nature on one side and an acidic nature of catalysts on the other [17,18]. To a certain extent, organic sulphur will be also incorporated in the coke. Heterocyclic rings will be the predominant form of N- and S-containing compounds. Phenolic structures and creosotes can also be present, especially after hydroprocessing of coal and biomass derived feeds. Special attention deserves the presence halogenated aromatic hydrocarbons. Thus, recent information indicates on attempts to apply hydroprocessing to the destruction of polychlorinated organic wastes [19]. Other organic wastes can also be included. Therefore, future applications of refinery catalysts should be carefully monitored, especially if the processing of organic wastes is being considered.

2.1.2. Hazardous characteristics of spent solid catalysts

The User's Guide [15] lists a dozen of hazardous characteristics. Those which may be applicable to the spent solid refinery catalysts are listed in Table 4. Some spent refinery catalysts can be classified as explosive and flammable solids as well as the substances or wastes liable to spontaneous combustion. According to the current RCRA regulations, a hazardous waste is defined as one that fails the tests for ignitibility, corrosivity, reactivity (cyanides and sulphides), or the Toxicity Characteristic Leaching Proce-

Table 4
List of hazardous characteristics [15]

Explosive
Flammable
Liable to spontaneous combustion
Corrosive
Toxic
Liberation of toxic gases in contact with air and water
Capable, by any means, after disposal, of yielding another material

dure (TCLP) [20]. Based on these regulations, spent hydroprocessing catalysts are classified as hazardous solid wastes, whereas FCC catalysts are non-hazardous. However, there is no guarantee that the current non-hazardous classification of the latter will not change in the future.

2.1.2.1. Hydroprocessing catalysts. The hazardous nature of hydroprocessing catalysts depends on the operating conditions. However, the procedure applied during the catalyst withdrawal from the reactor at the end of the operation can be even more important. If a proper procedure can be applied, the hazards can be significantly minimized. For example, if a hydroprocessing catalyst can be treated with either an inert gas or steam, and/or CO_2 in the absence of H_2 and feed, and at a near operating temperature, the amount of the carried over liquids can be substantially decreased. The amount of the entrapped volatile gases, which may include even H_2, can be decreased as well. Without a proper pretreatment prior to the catalyst withdrawal, the concentration of flammable vapours above the solid material may reach dangerous levels. In some cases, e.g. when special precautions were not taken during the catalyst withdrawal, it may be appropriate to classify the hazardous characteristic of spent hydroprocessing catalysts as that of the corrosive and flammable liquids. One information source indicates catalyst unloading under a vacuum [21]. It is stated that this method removes the catalyst without disturbing the operation, however, the type of catalyst and/or operation is not specified.

It appears that there is no safe catalyst withdrawal procedure which could be commonly accepted by all refiners. Refineries usually apply their own procedures. The need for a commonly accepted and/or approved procedure may develop in the future. In this regard, several patents describing the catalyst unloading techniques should be noted [22,23]. These techniques can significantly reduce or even eliminate the self-heating character of the spent catalysts. Otherwise, if spontaneous combustion begins, the inorganic sulphides and organic sulphur which are part of the spent catalysts may also contribute to the uncontrolled burnoff. In

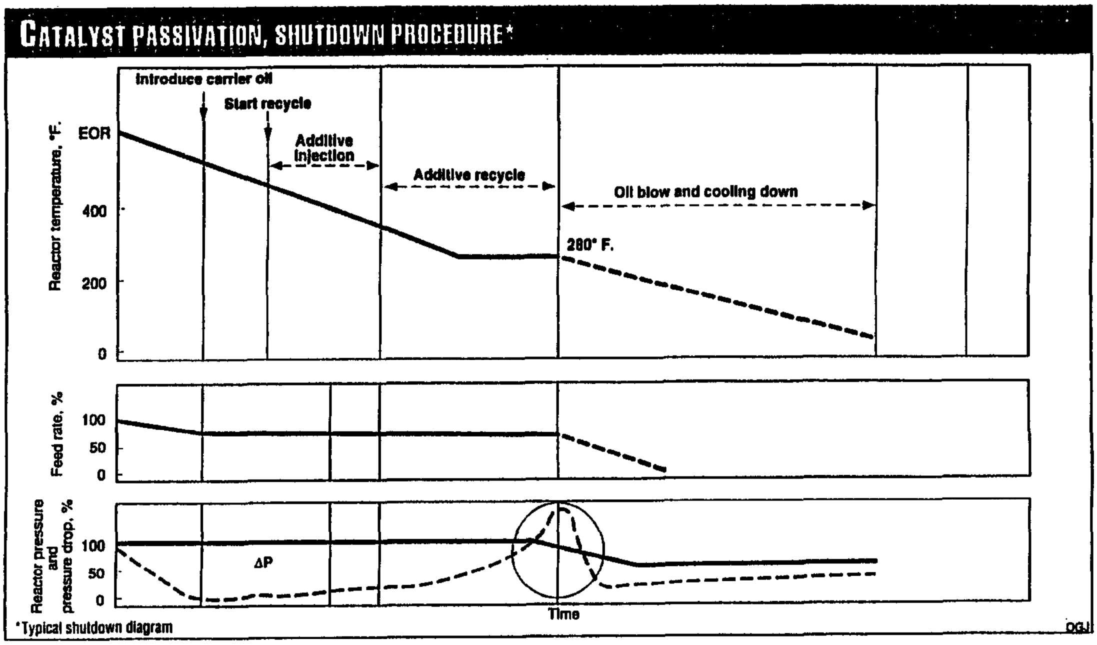

Fig. 4. Generalized procedure during withdrawal of spent hydroprocessing catalyst [24].

such a case, they will produce large quantities of SO_x. However, the inorganic sulphides alone require temperatures exceeding 200°C for spontaneous combustion to occur [4]. Part of the nitrogen in coke will be converted to NO_x during the spent catalysts burnoff [18], though the evolution of HCN and NH_3 is also possible.

New technology developed by Kashima Engineering Co., enables catalyst unloading after the operation under air rather than under an inert atmosphere [24]. This technology passivates pyrophoric or self-heating catalysts during the reactor shutdown by the application of a proprietary mixture of chemicals. The mixture contains compounds which deposit a film on the catalyst. This retards O_2 penetration, thereby suppressing oxidation reactions. A generalized shutdown procedure is outlined in Fig. 4. Initially, the feed rate is reduced by about two thirds while the reactor starts cooling down. When the reactor is below the reaction temperature, a carrier oil is introduced to display the feed. Once a carrier oil is put on a total cycle, a chemical inhibitor is injected and circulated for a required period of time. The unit is then cooled to about 140°C when recirculating oil is replaced by N_2 for further cooling to room temperature. The burnoff profile of the catalyst treated in this way is compared with that of an unpretreated catalyst in Fig. 5. Similar technique developed by CRI International [25] involves treating the spent catalyst with a mixture containing oxygen-containing hydrocarbons, having at least 12 carbons in the reactor prior withdrawal. These technologies may be applicable to both hydroprocessing and reforming catalysts. However, they may only have a limited application for spent FCC catalysts. More general applications may have the method based on the formation of a seal over the dry spent catalyst in the container [26]. The seal comprises a gelatinized starch. It is claimed that spent catalysts and other pyrophoric solids can be efficiently stabilized by this method.

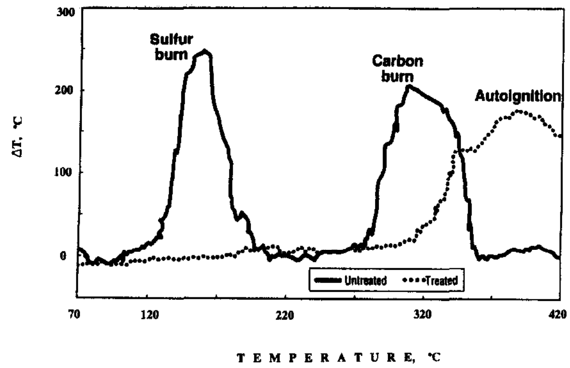

Fig. 5. Burnoff profile of pretreated spent hydroprocessing catalyst [24].

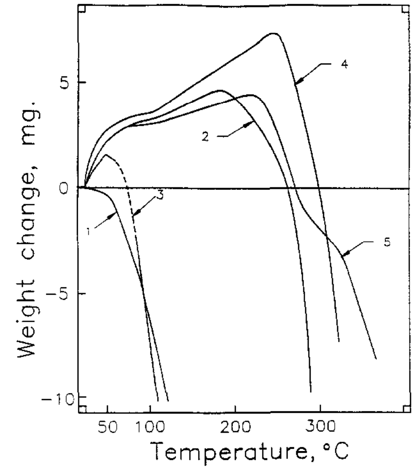

Fig. 6. Effect of pretreatment on ignition of spent hydroprocessing catalysts [27].

The results shown in Fig. 6 can be used to illustrate the effect of the pretreatment on spontaneous combustion for two hydroprocessing catalysts [27]. Curve 1 shows the weight change during the temperature programmed heating of the spent catalyst (as-received) in N_2. As expected, the weight decreased with increasing temperature. The same catalyst was pretreated at 200°C under N_2 and cooled to room temperature prior to the temperature programmed oxidation (TPO) in air. As curve 2 shows, the weight gradually increased due to O_2 chemisorption until the ignition temperature was reached. The TPO was performed on the same, but unpretreated catalyst. As curve 3 shows, in this case, the weight slightly increased and then rapidly decreased due to the ignition. Most likely, the ignition was caused by light fractions which otherwise could be removed by the pretreatment, as shown by curves 2 and 4. The latter involved the extraction of the spent catalyst by toluene, followed by treatment under N_2 at 200°C and cooling to room temperature prior to the TPO. It should be noted that the ignition of the unpretreated catalyst occurred at about 100°C compared with about 300°C for the pretreated catalyst. The beneficial effect of pretreatment on the catalyst ignition is also evident from curve 5, obtained for the second catalyst.

Another potential hazardous characteristic of the spent hydroprocessing catalysts includes the capability, by any means, after disposal, of yielding another material (e.g. leachates) and the liberation of the toxic gases in contact with the air and water. The EPA TCLP has been developed to determine the leachability of waste solids, such as spent hydroprocessing catalysts [28]. This procedure was applied to the evaluation of several commercial catalysts used in various hydroprocessing operations [29]. The results of these evaluations are shown in Table 5. It is evident that the leachability of some metals exceeds the level prescribed by the regulations. For example, a high content of As in the leachate from catalyst 1 deserves some attention. The high concentrations of the metals which are part of the fresh catalysts (e.g. Co, Ni and Mo) are rather evident. Among metals, which were deposited during the operation, V, As, Fe, Mn and Zn should be monitored. Some of these metals are not yet among the priority pollutants. It is however expected that they will be added to this list in the future. A significant difference in distribution of the hazardous pollutants among the tested catalysts is quite evident. This results from the difference in the composition of the treated feedstocks and processing conditions. Interestingly enough, some pollutants of a great concern (e.g. Pb, Hg, Cd, Se and Cr) were detected in very small (sub-trace) quantities only.

Table 5
Inorganic elements in leachates from TCLP of spent hydroprocessing catalysts [a] [29]

	Catalyst				
	1	2	3	4	Regulatory level
Al	*13.2*	*8.7*	*74.2*	*0.5*	
As	*53.3*	13	16	NA	*5*
Ba	7	63	NA	110	*100*
Be	0	5	6	NA	
Ca	*1.2*	*12.4*	*2.9*	*NA*	
Cd	NA	14	152	NA	
Co	*1.1*	*1.5*	*293*	*1.9*	*1*
Cr	14	38	NA	15	*5*
Cu	NA	NA	31	NA	
Fe	*3.4*	*81.6*	*15.2*	320	
Pb	317	258	413	93	*5*
Mg	*0.5*	*4.0*	*0.4*	*0.7*	
Mn	149	*1.9*	259	200	
Hg	NA	NA	4	NA	*0.2*
Mo	*249*	*8.7*	*310*	*3.0*	
Ni	*657*	*455*	*4.3*	*5.6*	
K	167	*2.4*	*1.8*	*0.7*	
Ag	NA	NA	NA	5	*5*
Se	1	4	NA	1	*1*
Sr	NA	315	19	NA	
Ti	19	25	31	30	
V	10	*205*	30	*8.4*	
Zn	244	*7.3*	258	160	

[a] Note: values in italic are in ppm; otherwise in ppb.

It appears that a more comprehensive approach is needed for establishing reliable database on leaching characteristics of spent hydroprocessing catalysts. Pretreating procedures which can decrease the leachability, can contribute to the solution of the problem. For example, the Maectite process, patented by Sevenson Environmental Services Inc. [30], is capable of converting reactive metals contained in solid wastes into non-leachable minerals in the apatite and barite group. These minerals are resistant to acidity and degradation by geotechnical and chemical conditions, such as those found in landfills and natural settings. The leachability of the unpretreated solid waste, and that pretreated using the Maectite process, is shown in Table 6. It is believed that the Maectite process can also be applicable to the spent solid refinery catalysts, although, so far, there is no published information to confirm it. Another approach which can decrease the leachability, is the encapsulation and stabilization of the spent

Table 6
Leachability (TCLP) of pretreated and unpretreated solid wastes [30]

	Concentration in leachate (ppm)		
	Unpretreated	Pretreated	Regulatory limits
Pb	5 to 3700	< 1	5
Cd	1 to 1596	< 0.1 to 0.7	1
Cr	5 to 660	< 0.3	5
Se	1 to 300	< 0.0025	1
As	≤ 4190	< 1.75	5
Ni	5 to 250	< 0.5	5
Ba	> 400	< 10	100

catalysts [31]. In case of the former, the spent-decoked catalyst is thermally treated with the organic substances such as bitumen, paraffin wax and different polymers. After cooling, the catalyst material is well sealed in the thermoplastic agent. However, long term effects of this method are not known. Also, some of these agents may be flammable. The stabilization involves a thermal treatment during which a spent catalyst is fused. This converts the leachable form of metals, such as Ni and Co, into a non-leachable form. An example of the stabilization method is the process patented by Phoenix Env. Ltd. [32]. In this process harmful constituents from hazardous wastes are converted to environmentally safe products by heating the waste in the flow of oxygen until the solid becomes a molten bath. After solidification, the molten bath has a spinel structure which can bond harmful species and convert them into a non-leachable form.

Besides the formation of leachates, the spent hydroprocessing catalysts, when in contact with the water, can liberate toxic gases. For example, due to the sulphidic nature of some parts of the mineral matter, the release of H_2S on contact with water can not be ruled out. Reliable experimental results on H_2S releases are not yet available, although there is some indication that this problem can be rectified by a pretreatment [33]. Thus, the sulphide sulphur in the spent catalyst can be converted to sulphate by treating the spent catalyst with a solution of hydrogen peroxide or exposing them in an open atmosphere. In the latter case, the progress of weathering is periodically checked and as soon as the oxidation is complete, the spent catalyst becomes non-reactive to the H_2S release.

Recently, a great deal of attention is being paid to the release of HCN and NH_3 from carbonaceous solids containing nitrogen in an inert atmosphere [34]. The coke deposited on the hydroprocessing catalysts is among such solids. In case of coal, the release of HCN and NH_3 during pyrolysis begins at about 350 and 500°C, respectively. Similar information on spent hydroprocessing catalysts was published only recently [35]. The results on the formation of HCN and NH_3 during pyrolysis and regeneration in 4% $O_2 + N_2$ balance of spent CoMo and NiMo catalysts are shown in Figs. 7 and 8, respectively. NH_3 is the main product in an inert atmosphere, whereas in the presence of O_2, the yield of HCN increased significantly.

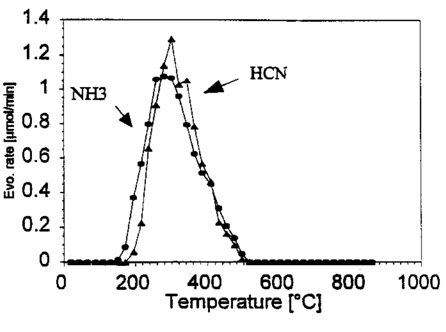

Fig. 7. Formation of HCN and NH_3 during oxidation of spent NiMo catalyst in 4% O_2 [35].

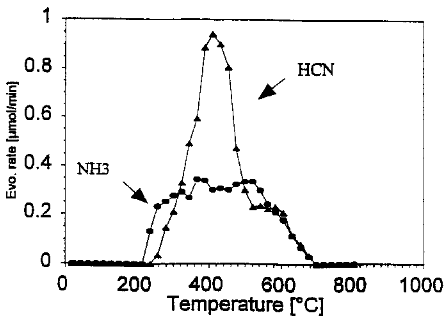

Fig. 8. Formation of HCN and NH_3 during oxidation of spent CoMo catalyst in 4% O_2 [35].

Table 7
Formation of HCN and NH_3 during thermal treatment of spent hydroprocessing catalysts [35]

	Yield (wt% of N in catalyst)		
O_2 conc. (vol%)	0	2	4
CoMo			
NH_3	9.9	11.9	11.4
HCN	0	15.0	16.4
NiMo [a]			
NH_3	14.4	11.5	8.7
HCN	0.5	7.8	8.4
NiMo [b]			
NH_3	7.8	9.8	7.2
HCN	1.9	9.2	11.0

[a] Extracted by hexane followed by toluene.
[b] Extracted directly by toluene.

The amount of coke's nitrogen converted to HCN and/or NH_3 is shown in Table 7. The mechanisms of HCN release in the presence of O_2 were discussed extensively [35]. In practice, there is a probability of HCN and NH_3 release while cooling the catalyst during and after catalyst withdrawal from the reactor. It is unlikely that such a situation may be encountered during storage and transportation, unless the sealed containers of the spent hydroprocessing catalysts are in the proximity of a fire environment. But this appears to be rather remote possibility. Nevertheless, the possibility for the release of very small quantities of HCN and NH_3 cannot be ruled out completely.

2.1.2.2. FCC catalysts. Some FCC units may generate as many as three different streams of spent catalysts. Although a continuous regeneration is an integral part of the FCC units, some of the catalyst must be removed downstream of the regenerator and replaced with a fresh catalyst to maintain steady catalyst activity. This solid waste stream is removed at the point following the regeneration, therefore the amount of remaining coke is very small. In addition to this, fines are removed from the regenerator off-gas using an electrostatic precipitator. These fines usually can not be reused in the refinery. The other portion of fines, passing the reactor cyclone may appear in the main column bottom as a clarified slurry oil. These fines can be recovered by cyclonic separators, otherwise, they will appear in the tank bottoms.

Refiners have been making continuous efforts aimed at additional environmental improvements to the FCC operations. For example, particulate emissions of the advanced FCC units are 90% less than that of the first FCC units [36]. Currently, particulate emissions of FCC catalyst dust in the stack is for most units under the NSPS standard of 1 lb/1000 lb of coke burn. It is anticipated that the current NSPS particulate standard may be reduced to about 1 lb/3000 lb of coke burn in the near future. Further improvements are among the objectives of the refinery operators. In this regard, the US idea for the joint government/industry operation of a user FCC unit deserves some attention [37]. This facility can be used by any refinery for process and environmental R&D to improve performance of the FCC units and to ensure that the produced solid wastes are non-hazardous. Such a facility can be part of an

Table 8
Content (wt%) ranges of some metals in spent FCC catalysts [38]

	Maximum	Minimum
Antimony	0.1600	< 0.0001
Arsenic	0.0185	< 0.0001
Beryllium	0.0004	0.0003
Bismuth	0.1700	< 0.0001
Boron	0.7410	< 0.0001
Chromium	0.0678	0.0005
Copper	0.0066	0.0003
Iron	0.0500	0.2300
Lead	0.0140	< 0.0001
Nickel	1.4000	0.0210
Phosphorus	2.2000	< 0.0001
Selenium	< 0.0100	< 0.0001
Silver	0.0059	< 0.0001
Strontium	0.0505	< 0.0001
Sulphur	0.6710	0.0025
Tin	< 0.0100	< 0.0001
Titanium	1.2500	0.0171
Vanadium	0.7000	0.0310
Zinc	0.0315	< 0.0001

Table 9
Inorganic elements in spent FCC catalysts and corresponding TCLP leachates [38]

	Catalyst			Leachate	
	A	B		A	B
ppm					
Pb	12	350		0.07	0.15
Sb	290	< 5		0.72	0.01
V	2470	552		4.1	0.52
Ni	860	740		0.6	0.25
Ag	< 1	< 1		0.02	0.01
Cu	22	105		NA	NA
Hg	< 1	< 1		0.05	0.05
Cd	< 1	< 1		0.01	0.01
Se	< 1	< 1		0.02	0.015
As	< 1	< 1		0.03	0.025
wt%					
BaO	1.3	0.02	Ba	2.4	0.13
Cr_2O_3	0.01	0.02	Cr	0.01	0.02
Al_2O_3	34.6	37.3	Al	1.5	2.4
SiO_2	61.3	60.2		NA	NA
Fe	0.31	0.81	Fe	0.7	0.9

integrated refinery acquired and/or subcontracted for this purpose.

The flammability of the spent FCC catalysts is significantly lower than that of the spent hydroprocessing catalysts because of a more refractory nature of the deposited coke, i.e. much lower H/C ratio. Also, the amount of coke on the spent FCC catalysts is much lower. However, this coke is finely distributed on a large surface area thus being readily accessible for oxidation. Nevertheless, it is unlikely that the spent FCC catalysts will ignite during withdrawal and handling, if all usual procedures are applied.

Pavel and Elvin [38] reported concentration ranges of 39 metals in the spent (equilibrium) FCC catalysts. Some of these metals are listed in Table 8. However, the TCLP applied to the fresh, spent, fines and demetallized FCC catalysts confirmed that a hazardous designation for these solids is not warranted [39]. This is also confirmed by the results in Table 9, showing the content of priority elements and other metals in the leachates after applying the TCLP test. As one would expect, the content of metals in the leachates depends on their content in the spent FCC catalysts. The TCLP test was also performed on the crushed bricks prepared from a mixture containing 5 wt% of the spent FCC catalyst [12]. As the results in Table 10 show, these bricks were virtually non-leachable with respect to V, Ni and Sb.

The leachability of the spent FCC catalysts deserves continuous attention in spite of being currently classified as non-hazardous solids. The significantly lower content of deposited metals, compared with the spent hydroprocessing catalysts, may be a misleading criterion. Thus, a relatively small amount of coke and a much smaller mean particle diameter of the FCC catalysts favour high leaching rates. Further, the development of new FCC catalysts, more tolerant to V and Ni, may produce spent FCC catalysts which may not pass the TCLP test. The introduction of new techniques for separation of a heavy metal deposited portion of the spent FCC catalyst from the active portion may yield a solid waste, which in content of V and Ni may approach that of spent hydroprocessing catalysts [40]. Nevertheless, some concerns about the leachability of the spent FCC catalysts are being expressed, though no results were given to indicate on their hazardous nature [12].

Table 10
Leachability of crushed red brick containing 5 wt% of spent FCC catalyst [12]

	Conc. in brick (mg/kg)	Conc. in eluate (mg/l)	Eluate criteria (mg/l)	
			US	EC
Sb	8	< 0.005	15	
Cu	51	0.115	25	10
Ni	94	0.010	20	2
V	227	0.134	24	

2.1.2.3. Reforming catalysts. Among solid refinery catalysts, the information on hazardous characteristics of reforming catalysts is the most limited. This is understandable considering the price of precious metals which are part of these catalysts. Thus, all necessary precautions to minimize losses and to avoid any damage which would complicate a full recovery of the precious metals are being routinely applied. Nevertheless, the presence of coke may indicate on some flammability of the spent reforming catalysts, especially if not all precautions are taken during catalyst withdrawal from the reactor, i.e. the flammability can be enhanced in the presence of light carryovers [41]. Also, a reduced form of the Pt group metals is believed to be sensitive to the air and moisture. The TCLP leachability of reforming (fresh, regenerated and spent) catalysts is perhaps the least documented compared with hydroprocessing and FCC catalysts. The same procedures used for controlling the flammability and leachability of spent hydroprocessing catalysts may also be suitable for the spent reforming catalysts.

2.1.2.4. Other catalysts. Besides typical refinery processes, such as hydroprocessing, FCC, reforming and alkylation, other catalytic processes may be part of the refinery operation. In most cases, the volume of miscellaneous catalysts represent only a fraction of the total volume of the typical refinery catalysts. Some refineries are producing H_2 by steam reforming of hydrocarbons. This involves two catalytic steps, i.e. steam reforming and water–gas shift. The catalyst used in the first step may contain up to 20% Ni combined with various supports. The Cr-promoted Fe oxide is a typical high temperature shift catalyst, whereas the Cu-Zn/Al_2O_3 is a typical low temperature shift catalyst. H_2S, a common by-product of several refinery processes, is converted to elemental sulphur in the Claus process employing catalysts such as Al_2O_3, TiO_2 and others. The removal of SO_2 from tail gases from Claus plant requires the use of a catalyst as well. In this case, an activated Al_2O_3 and/or Al_2O_3 combined with Mo, Co or Fe can be used. Refineries performing the H_2SO_4 regeneration on-site have to use an oxidation catalyst, such as V_2O_5 to convert SO_2 to SO_3. Recent trends indicate on the addition of various petrochemical units to the refinery site. This may further expand list of the catalysts being used on the same site. With respect to the hazardous characteristics, each catalyst has to be evaluated independently. The chemical composition of the catalyst is the basic information needed for such evaluation. Of course, catalysts containing some regulated species, e.g. Cr or species which may be regulated in the future, e.g. Ni, V, Zn and others will require more attention than those which do not contain regulated elements. In view of the catalyst diversity, this review will focus only on typical refinery catalysts.

2.2. Classification of regenerated and fresh solid catalysts

Solid regenerated and fresh catalysts are non-flammable and non-toxic materials. They do not require a high level of environmental and safety awareness. Thus, the protective items usually used by the operators of refinery units should be adequate. Perhaps, the exposure to the dust during loading and unloading of the catalysts may require some attention, as indicated by Hery et al. [42]. This may be the case especially for the spent FCC catalysts because of a high content of fines. Of course, solid regenerated and fresh catalysts are leachable. However, only in some accidental situations (e.g. erroneously disposed) these catalysts can be a cause of an environmental hazard because of their leachability.

2.2.1. Regenerated catalysts

Regenerated catalysts contain no organic and/or combustible contaminants. These were all removed during regeneration. This includes most of the inorganic sulphur and nitrogen. However, a small amount of sulphur may still be present as sulphate. A small amount of nitro-

Table 11
Typical analysis of spent-regenerated hydroprocessing catalysts (wt% on a calcined basis) [44]

	A Co-Mo	B Ni-Mo	C Ni-W	D Co-Mo	E Co-Mo
Al	35	33.1	17.7	32.5	28
Mo	8.8	12.3	0.47	6.4	6.2
V	1.2	0.05	< 0.04	2.6	10.5
Ni	0.3	2.6	2.5	0.49	3.1
Co	3.2	< 0.04	< 0.05	1.6	2.1
W	< 0.05	< 0.05	15.2	< 0.05	< 0.05
Pb	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Si	0.5	0.3	13.2	0.3	1.2
Fe	0.21	0.12	0.18	0.29	0.7
As	< 0.05	< 0.05	< 0.05	0.2	0.4
P	< 0.05	3.2	0.2	< 0.05	< 0.05
Na	0.2	0.03	0.04	0.13	0.5

gen, presumably as a metal nitride, can also be present [43]. All remaining metals and metals which were deposited during the operation are in various oxidic forms. Typical analyses of the regenerated hydroprocessing catalysts are shown in Table 11 [44]. Catalysts A and D are CoMo catalysts slightly contaminated with the V and Ni, whereas catalyst E is heavily contaminated by these metals. Relatively large quantities of As are present in catalysts D and E. Catalyst B is a typical hydrodesulphurization catalyst containing phosphorus which was probably added during catalyst manufacture as the passivating agent. Catalyst C is a hydrocracking catalyst containing silica–alumina as the support. Other catalysts in Table 11 contain alumina as the support.

The composition of regenerated catalysts from FCC and reforming operations approach that of the fresh catalysts. In case of FCC units, the catalyst is continuously regenerated and most of it is returned to the operation. Therefore, even a potential leachability of regenerated FCC catalysts becomes a non-issue. For obvious reasons, both the refiner and regenerator are taking all necessary precautions to recover all regenerated reforming catalysts. Also, in this case, a situation in which the leaching of metals could be of a concern is difficult to imagine.

2.2.2. Fresh catalysts

Similarly as the regenerated hydroprocessing catalysts, leachability is the only characteristic which should not be completely ignored. The same methods can be applied for the handling of both regenerated and fresh catalysts. Perhaps, developments in the catalyst design deserve some attention. For example, some refiners prefer to use the catalyst which was presulphided by the manufacturer [45]. In this case, handling of the catalyst should take into consideration the presence of metal sulphides. Also, fluorine is sometimes added to the hydroprocessing catalysts to improve their performance. It is anticipated that other species may be added to fresh catalysts.

Handling of the fresh FCC catalysts should take into consideration the presence of passivators such as phosphorus, tin and antimony. For the fresh FCC catalysts, the presence of fines, although in very small quantities, may require the use of protective items during their handling to avoid respiratory problems [36,42].

2.3. Transportation of catalysts

According to the Basel Convention, the international shipment of hazardous wastes between developed and developing countries is illegal [46]. The US is perhaps the largest exporter of wastes in the world. These exports are regulated by the EPA regulations which require a waste-receiving country to certify its willingness to accept hazardous waste exports before they are shipped. The Transportation of Dangerous Goods Act (TDGA), in effect in North America, requires that all shipments of dangerous goods and hazardous wastes are accompanied by a declaration, referred to as a manifest. The TDGA regulations are being applied for the transportation of spent catalysts. In the European Community, transportation of spent catalysts is subject to two different regulations, i.e. the ADR (Autorization/Dangerous/Road) code and the IMDG (International/Maritime/Dangerous/Goods) [11]. The latter covers shipping of catalysts overseas, whereas the ADR applies to the road transport within the EC.

The regulations require that all safety precautions are taken during the transportation of hazardous wastes. For example, the packaging and/or containers must ensure an adequate sealing to prevent contact with water and air, as well as the leakage of gaseous and liquid constituents of a hazardous nature into the environment. The choice of packaging is directly related to the classification of the spent catalysts [15]. Because they are classified as hazardous wastes, spent hydroprocessing catalysts require much more attention than other spent solid refinery catalysts. Their flammability and leachability dictate that they cannot be shipped in supersacks or in bulk. If there are more than one catalyst, it is essential that the catalysts are segregated and properly labelled. For this purpose, a container which is specially approved by the environmental authorities would be required. The use of metal containers appears to be the most suitable packaging method provided that they have undergone tests for resistance to impact and tightness, as prescribed by the United Nations (UN) texts and that they are labelled accordingly [44]. The companies, who can perform all packaging and transportation services, require special certification from the environmental authorities. The transportation of regenerated and fresh catalysts requires less attention, but the catalysts should still be properly labelled and any contact with water should be avoided.

Transporting large volumes of the spent H_2SO_4 from the alkylation units to the regenerator and back has significant potential risks. The current trends indicate a growing interest in the on-site regeneration of the spent acid to avoid such a risk. Because of significantly different properties, procedures applied during transportation of HF are much more demanding than those during transportation of H_2SO_4.

The transboundary movement of the spent hydroprocessing catalysts is controlled by the regulations on the Export and Import of Hazardous Goods [15]. These regulations set conditions which should be met before spent catalysts can be imported in, exported or transited through a country or a province. All persons and companies involved are required to notify the appropriate authorities in advance, i.e. one year before the proposed shipment. An example of the required information (notice) is shown in Table 12. For the export from a country, the generator/exporter is responsible for completing the notice. For imports, the recycler/disposer/importer is required to provide the country's authorities with the notice. In case of the shipment that will only transit the country, the notice should be completed by the carrier.

Table 12
Export/import information [15]

Exporter/foreign generator
Foreign receiver/importer
Carrier
Final destination
Number of imports/exports
Customs offices
First export or import
Transit countries
Hazardous waste information
 – International waste identification code (IWIC)
 – ID number
 – TDGR product identification number (PIN)
 – Primary TDGR hazard class
 – Quantity of waste
 – Packing group and type
Special handling instructions
Undertaking of the exporter
Certification and signature

2.4. *Storage and/or disposal of spent solid catalysts*

A continuous change in environmental regulations will also have an impact on the methods used for handling, storage and disposal of spent refinery catalysts. The focus will be on the parameters determining the impacts to the landfill and landfill operators, mobility of potentially hazardous constituents and adverse health effects associated with the waste. It may be appropriate to accept these changes as part of everyday life. Thus, refiners should be prepared to make some adjustments and/or be ready to respond timely to these changes. Nevertheless, in spite of the significant efforts to bring the storage and disposal of spent solid refinery catalysts under control, there still might be some cases of an irresponsible dumping even that of the hazardous wastes such as spent hydroprocessing catalysts [47]. Such unauthorized dumping should give a rise to concern. This situation can be rectified either by developing suitable pretreating, storing and disposal techniques to minimize environmental hazards or by implementing relevant laws to completely eliminate all cases of unauthorized dumping. Owing to greater environmental awareness, some refiners store spent catalysts on site, awaiting time when better treatment techniques will be available. However, this kind of the storage is again only a temporary solution and at some point it may attract the attention of the environmental authorities.

Several methods which may be suitable for the storage and disposal of spent solid refinery catalysts can be identified in the User's Guide [15]. For example, specially engineered landfilling, such as placement into the separate lined cells capped and isolated from each other and the environment, appears to be applicable. Another option which deserves some attention involves longer term storage, such as placement of the containers in mines. But this could also be only a temporary solution. There may be a need for temporary, short term storage, especially in the case when the fate of spent catalysts must still be determined by analysis. For this purpose, carefully maintained storage in polypropylene supersacks may be adequate.

The determination of hazardous characteristics, especially leachability, flammability and toxicity of the spent catalysts, should be an essential requirement before choosing the procedure for storage and/or disposal. In the long term, this may prove to be cost efficient. The concept of the joint liability suggests that if something goes wrong with an unsecured landfill within 20 years of the disposal, e.g. ground water contamination, the company may be asked to cover the entire cost of the clean-up [48]. Then, a catalyst, or any other waste could be disposed of into a landfill only if it can be proven with certainty that the landfill meets all non-hazardous criteria.

According to the American Petroleum Institutes refining solid waste survey conducted in 1982, about 70% of the non-regenerable catalysts were disposed of in commercial landfills [49]. Some of these landfills were probably operating under the RCRA interim status permit. The RCRA amendments issued in 1984 required all interim status hazardous facilities to meet ground water and insurance requirements. For continued operation, minimum technology of a double liner and leachate collection system was required to be installed by 1988. Many refineries responded by replacing all surface impoundments with the above ground tankage [50]. After closure, the contents of the impoundments were emptied, the contaminated soil removed and the impoundment filled. It was felt that it was worthwhile to take such a costly approach to avoid the possibility of repairing a leaking liner in the future. There are some indications regarding the reauthorization of the RCRA which will require that most of the surface impoundments are retrofitted or closed by 1995. Also, additional waste streams will be added to the current list. The Comprehensive Environmental Response, Compensation and Liability Act may result in a possible loss of exclusion. This could subject the refining industry to a cleanup anywhere the spent refinery catalysts have been disposed of in the past.

Syncrude Canada Ltd. can be taken as an example of how the disposal problem can be minimized. This company has been generating spent catalysts containing Mo, Ni, Co, Cu, Zn and Fe [51]. To avoid landfilling, these catalysts are being shipped to two smelters, one recovering Mo, Ni and Co and the other Cu and Zn. The choice was based on the environmental impact studies which revealed that both smelters had a track record as good corporate citizens and were experienced in handling similar materials. The catalysts were contained in the single-trip drums with bolted hoops. This packaging was approved by the environmental authorities. The other refinery sends spent catalysts to a special waste treatment center for disposal [52]. This center operates a landfill with the double liners, leachate collection and ground water monitoring systems.

An environmentally conscious company involved in metal reclaiming from spent catalysts published the approach used to ensure that all regulations are complied with [53]. The company has been using a fully permitted hazardous waste bulk storage pad designed to prevent run-on, run-off and to handle all drainage according to the EPA regulations. Before constructing a new metal recycling plant, the company has commissioned a third party environmental audit of the plant situated near the Mississippi River. The previous site operations were also included in the audit, which lasted six months. The audit included the evaluation of the potential impact on groundwater and soil contamination, as well as a review of the permit status and files to assess potential liability of the site. In summary of this audit, a shallow, confined, permeable deposit was discovered about 10 m under the previous site. This zone was confined by clays and silts. The water samples taken from it revealed that all metals were at the background level or that of the river. The new plant was constructed on top of a very tight formation of clays and silts having very low permeabilities.

2.4.1. Hydroprocessing catalysts

One source of information suggests that between 15 000 and 25 000 tons of spent hydroprocessing catalysts are stored at various places around the world [47]. These catalysts can be regarded as recoverable. A further 10 000 tons is known to be dumped unpacked and should be considered to be non-recoverable.

The number of reports on disposing the spent hydroprocessing catalysts in the unapproved landfills was waning, and in the most recent years, no information indicating such a landfilling appeared in the literature. This may be understood considering the level of hazard which such wastes pose to the environment. In fact, Habermehl [54] rightly states that because of potential future liabilities, disposal in unapproved landfills is the worst alternative. Many refiners were taking necessary precautions well before spent hydroprocessing catalysts were included by environmental authorities among the hazardous wastes. Thus, they were already disposing of the spent catalysts in approved landfills designed and operated to prevent ground water contamination.

2.4.2. FCC catalysts

Worldwide usage of FCC catalysts, and thus a total production of the spent FCC catalysts may approach 400 000 tons annually [3]. About 10% of spent FCC catalysts are in the form of catalyst fines. It is reasonable to assume that most of the regulations applicable to spent hydroprocessing catalysts can be also applicable for the disposal and storage of spent FCC catalysts. Lesser contamination of the latter should not be a reason for a more relaxed approach to the solution. Thus, although spent FCC catalysts are currently classified as non-hazardous, it is certainly likely that their disposal will be regulated in a future. The regulations may take the form of some maximum level of metals on the spent catalyst which can be put into landfills [36]. This level would be based on a standardized leaching test. A detailed analytical evaluation prior to storage and/or disposal should also be essential for spent FCC catalysts. For example, catalyst fines may be handled differently than the spent (equilibrium) FCC catalysts.

According to the article published by Corbett in 1990 [55], the spent FCC catalysts were disposed of in sanitary landfills or sold to other refineries who used them in less severe operations. It was indicated that disposal in landfills requires pretreatment to avoid the spent FCC catalyst and especially catalyst fines flying around. Also, some lime had to be added to keep the pH of the ground water within the acceptable limits. The information from the 'final cascader' or end users of the spent FCC catalysts is limited. It is reported [56] that in one case, a 'final cascader' was accumulating spent FCC catalysts on the property for several years since the nearby non-hazardous landfill would not accept it, even though the material was classified as non-hazardous based on the EPA TCLP test. The dry disposal or disposal in land farms was not acceptable without a pretreatment. The best solution was to sell spent FCC catalysts to cement kilns as a source of alumina. However, some refiners are concerned that the cement manufacturers will be taking the spent FCC catalyst only as long as they are classified to be non-hazardous.

The European approach to handling spent FCC catalysts was described by Schmitt in 1990 [12]. It appears that landfilling will become increasingly difficult and costly with possible associated liabilities. In some cases, treatment prior landfilling may be necessary, thus adding to the cost. The refiner, who is identified as the producer of the waste, is responsible until the waste is given to the authorized disposal facility. Thus, the refiner may be liable for the damage caused by the third party, such as the transporter of the spent FCC catalysts. The refiner may be liable if the spent FCC catalysts were not sent to the licensed disposal site, even if he has no operational control over the waste.

2.4.3. Reforming catalysts

The refiner makes all possible efforts to regenerate the spent reforming catalysts for reuse. Only temporary storage may be required for the non-regenerable catalysts. In this case, procedures applied for handling of the spent hydroprocessing catalysts (prior to their regeneration) may be adequate. Considering the high price of the precious metals, it is unlikely that the non-regenerable reforming catalysts will be stored for a long period of time before they are shipped for metal reclamation.

3. Management of acid catalysts

Acids, such as HF, H_2SO_4 and H_3PO_4 are being used as catalysts for alkylation and polymerization. With respect to safety and the environment, these technologies, alkylation in particular, are rather unique. It is fair to state that no other technology, used in refinery requires more attention than alkylation. It is believed that a separate Section devoted to these issues appears to be a necessary part of this review.

The alkylation process combines olefines (C_3, C_4 or C_5) with isobutane in the presence of acid catalysts such as HF or H_2SO_4, to high octane number iso-paraffins. The C_3 and C_4 olefines can also be converted to more valuable higher molecular weight gasoline fractions using polymerization. Typical polymerization catalysts comprise phosphoric acids supported on silica or diatomaceous earths. Both alkylation and polymerization have been gaining in importance because of a growing demand for the reformulated gasolines, of which the contribution to the gasoline pool has been steadily increasing.

Isomerization may be an integral part of the alkylation systems. In this case, *n*-butane produced in other parts of the refinery is isomerized to iso-butane which is then used as the feed for the alkylation. Higher *n*-paraffins can also be isomerized to iso-paraffins with aim to increase octane number of the straight run distillates. Isomerization catalysts generally comprise the platinum group metals combined with Al_2O_3. The presence of the precious metals suggests that handling of the isomerization catalysts will be identical as that of the reforming catalysts, which will be discussed in the last parts of the review.

The alkylation technology using HF and/or H_2SO_4 acid catalysts was reviewed in detail by Albright [57]. Typical temperatures employed in HF and H_2SO_4 processes are 30 to 45°C and about 5°C, respectively. Thus, for the latter, a special cooling system has to be used, whereas for the HF processes, cooling water may be adequate. The agitation is also very important to ensure efficient contact between the acid and hydrocarbon phases. Because of a lower viscosity, efficient contact may be achieved more readily for the HF processes. The isobutane/olefin ratio is always higher for HF units than that for H_2SO_4 units.

The acid alkylation catalysts, HF in particular, have been attracting continuous attention from environmental authorities. It is predicted that new alkylation units will be using H_2SO_4. Also, there are some trends indicating the conversion of HF units to H_2SO_4 units. At least in the short term, the consumption of H_2SO_4 in alkylation is expected to grow.

Tightening of environmental and safety requirements forces the industry to develop new alkylation technologies. In the long term, both HF and H_2SO_4 will be facing tough competition from new alkylation catalysts. In this regard, the focus is on solid and/or solid supported acids such as aluminum chloride, antimony pentafluoride, alumina–zirconium chloride and others [58]. It is expected that solid acid alkylation units will have the greatest impact on HF alkylation and eventually replace all HF units.

3.1. Hazardous constituents and characteristics

All forms of the currently used alkylation catalysts, i.e. fresh, regenerated and spent are classified as toxic and corrosive materials [15]. In fact, they can be fatal to humans if they are inhaled or ingested, or if they penetrate the skin. After penetrating the tissue, HF can react with calcium and magnesium in the blood and cause hypocalcemia. They can also cause reversible and irreversible damage when in contact with the living tissues.

There is also a chance of the liberation of corrosive fumes when in contact with the air and water. Although most of the attention is focused on HF, some refiners believe that the HF and H_2SO_4 processes are more or less equivalent on a safety basis [59]. This is supported by the immediately dangerous to life or health levels for the priority species published by EPA, i.e. HF 30 ppm, SO_2 100 ppm and H_2SO_4 in the form of the mist 20 ppm. Levels for the emergency planning guidelines are 50, 15 and 7 ppm for HF, SO_2 and H_2SO_4 mist, respectively.

Contamination of acids during alkylation increases their potential for hazards. In the case of H_2SO_4 processes, presence of a sulphonated product in the spent acid deserves much attention. This is supported by the results published by Sung et al. [60]. Thus, the spent H_2SO_4 can release SO_2 due to the presence of a polymer contaminant according to the following reaction:

$$H_2SO_4 + CP = SO_2 + 2H_2O + CP'$$

where CP is a polymer formed during alkylation, and CP′ is the same polymer which has lost a hydrogen. Thus, the CP′ may contain a double bond. This could be favourable for the reaction of CP′ with H_2SO_4 leading to the unwelcome sulphonation products. These reactions deplete H_2SO_4 which then must be compensated for during the regeneration. Also, if no precautions are taken, the SO_2 may be released to the environment. In an enclosed container, a pressure build-up may occur causing dangerous situations. As the results in Figs. 9 and 10 show,

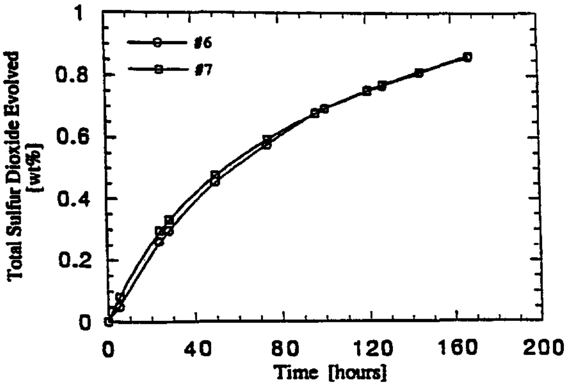

Fig. 9. Evolution of SO_2 from spent H_2SO_4 acid at 40°C [60].

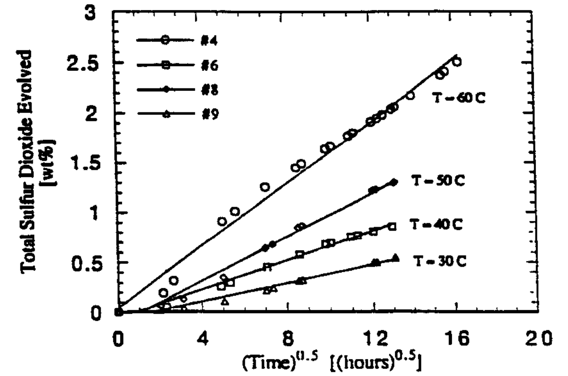

Fig. 10. Effect of temperature on evolution of SO_2 from spent H_2SO_4 acid [60].

the amount of evolved SO_2 depends on the time and temperature, respectively.

3.2. Disposal and utilization

It is again emphasized that because of the limited disposal options and rising costs, the recovery of the spent HF and H_2SO_4 acids, as complete as possible, is the primary objective of the refiner. In the past, spent acids were neutralized and discharged into waterways or injected into deep wells. It appears that discharge permits are being phased out in many countries [61]. Also, the authorities are now paying more attention to deep well injections. New disposal procedures will have to be developed unless complete recovery/utilization of the spent acids can be achieved. A caustic treatment of alkylation products to remove remaining acid generates additional solid waste. It was reported that in case of caustic potash, generated potassium fluoride was usually dumped [62]. But this method was of concern to those involved. Spent polymerization catalysts represent a complex mix of catalyst, tar and coke. It was suggested that these catalysts are non-hazardous and as such, can be landfilled [63].

In the past, some portion of the spent H_2SO_4 could be sold to the fertilizer producers who used them to dissolve phosphate ores [61]. Health concerns, a depressed fertilizer market and tightening disposal regulations for the gypsum by-product have dried up this option. In alkylation units employing HF, the activated alumina is used to remove fluoride from hydrocarbon streams. The spent alumina, referred to as fluorinated alumina, is a mixture of AlF_3 and unreacted Al_2O_3. This non-hazardous solid has been traditionally landfilled until a vendor initiated a program to reuse this material at an aluminum production plant, where AlF_3 is a necessary ingredient for conversion of the alumina to aluminum metal [63]. In this case, the fluorinated alumina is used as a substitute AlF_3, which is otherwise purchased commercially. In the case of one refinery [64], about 180 metric tons of fluorinated alumina will be reused in this manner annually. This application generates cash besides eliminating costs and potential future liabilities, which could result from landfilling. There is a need for new safe procedures for the disposal and utilization of the spent acids or by-products which cannot be regenerated for reuse.

The spent polymerization catalysts comprise a complex mixture of catalyst and polymer. This mixture is non-permeable and its removal from the reactor is rather labour intensive [65]. However, the presence of phosphorus makes spent polymerization catalysts an attractive source of phosphorus for the fertilizer production. According to Spearman [63], one refinery sells about 160 metric tons of the spent polymerization catalyst annually to a fertilizer producer. This decreased handling costs of the waste in the refinery.

3.3. Mitigation

In recent years, the general public and governments have been increasingly concerned over the potential of accidental releases of hazardous materials. In this regard, the currently used alkylation acid catalysts have attracted a great deal of attention. Both the HF and H_2SO_4 plants contain a large inventory of the concentrated acid. Both these acids can cause serious injuries to people directly in contact with them. However, the difference between the properties of

Table 13
Physical properties of fresh acids [66]

	HF	H_2SO_4
Acid strength	100	98
Vapour pressure at 25°C (psia)	17.6	4×10^{-6}
Boiling point	19.4	329
Freezing point (°C)	−83	0.5
Viscosity at 10°C (cP)	0.23	40
Surface tension at 20°C (dyn/cm)	8.6	55.1

these acids, shown in Table 13 has a distinct impact on the mitigation effort [66].

It is believed that one issue which has a significant impact on the safety of alkylation processes, i.e. the safe handling of large amounts of the highly explosive hydrocarbon mixture, is being frequently overlooked. It is believed that this issue deserves at least the same, if not more, attention than the acids. To prevent accidents involving such mixtures may be as important as all safety precautions taken to prevent releases of the acids.

3.3.1. HF processes

Because of its volatility, HF can form a vapour cloud if spilled. It is also capable of forming an aerosol cloud. Both the vapour and aerosol can cause a serious inhalation hazard. The release of superheated HF will result in the formation of a cold dense vapour cloud or aerosol, which may persist for a long distance. Attempts have been made to develop an additive that can reduce formation of the HF aerosol. Besides decreasing the aerosol formation, such an additive should have little effect on alkylation and be stable during the all stages of processing. In this regard very promising results were obtained with the alkylation process carried out in the presence of a liquid onium polyhydrogen fluoride complex [67]. This complex is produced between an additive and HF. The vapour pressure of the HF-complex is significantly lower than that of the anhydrous HF. As the results in Fig. 11 show, aerosol formation can be significantly reduced by the additive [68].

In spite of the significantly higher toxicity of HF compared with H_2SO_4, there are currently about half of the alkylation units in the USA and other parts of the world, which are still using HF as the alkylation catalyst. For this purpose, specially designed systems are used for storing the acids used in alkylation. One infor-

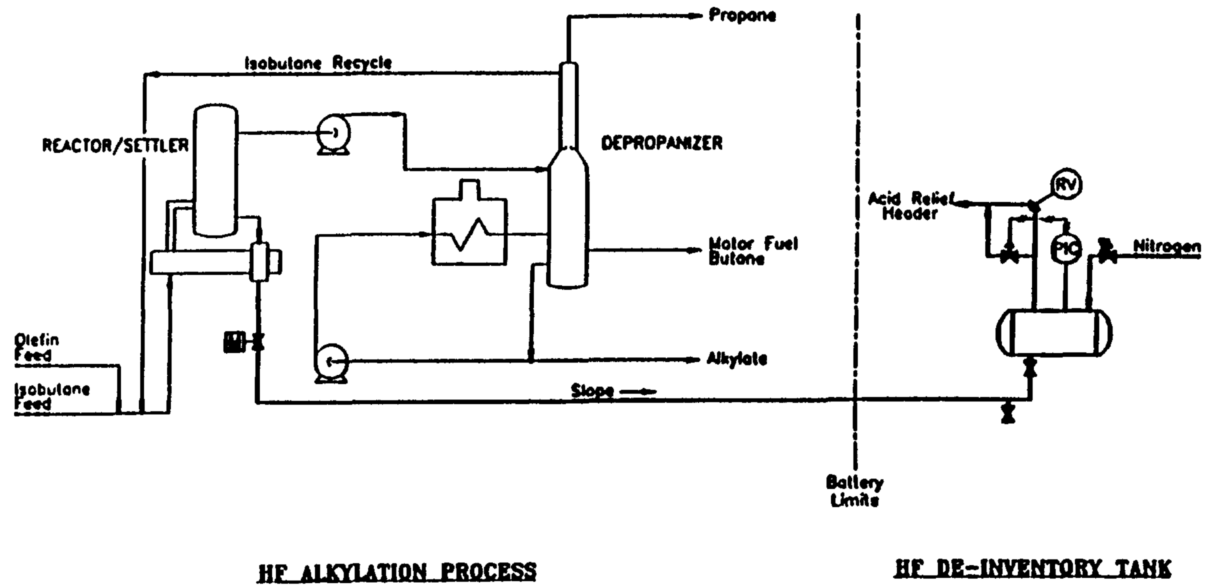

Fig. 12. Process flow schematic of HF mitigation system [69].

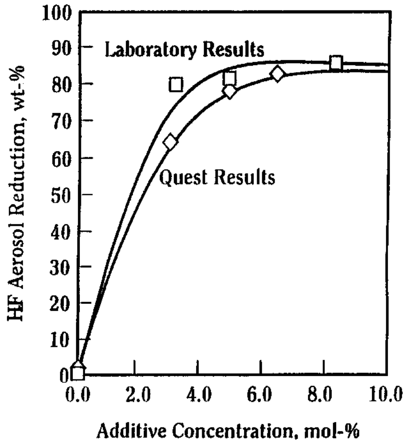

Fig. 11. Effect of additive concentration on reduction of HF aerosol formation [68].

mation suggests that for the HF case, the acid storage system stores all acid inventory in three different locations, such as the acid storage drum, reaction section of the alkylation unit and the acid dump drum [67]. In the event of a leak, the acid storage system can remove the acid from the unit. Perhaps, the best account of the HF emergency de-inventory system was given by Stewart and McVey [69]. The concept of the de-inventory system which is part of the alkylation unit is shown in Fig. 12. The time required to detect the leak and to empty the leaking container to safe storage is an essential consideration. Accurate location of the leak may be time consuming. This depends on the amount of acid fog and water mist generated during the leak. For this purpose, strategically located leak detectors could significantly improve the situation. Sensitive detectors are now available, which can detect HF in sub-trace quantities [70]. The vessels which are unlikely to be involved in a leak scenario, i.e. acid storage drum, may be isolated from the de-inventory system. The displaced gas and vapour generated by the de-inventoried acid must be vented from the receiving vessel. Because they contain both HF and hydrocarbons, they should be scrubbed with caustic and vented to a flare system.

Frequent testing of the de-inventory system for its reliability should be carried out. Thus, the reaction of HF with carbon steel can impact the safety and reliability of the HF units by promoting formation of the hydrogen blisters in the carbon steel pressure vessels [71]. Also, HF has the tendency to wet H_2S and to promote various forms of hydrogen induced cracking. These effects may cause malfunctioning of some components of the system. The reliability of all instrumentation, which is part of the de-inventory system, should also be periodically verified. As stated by Scott [66], it is essential that every refinery, operating the HF alkylation unit has the set of clearly defined procedures for cleaning, neutralizing and disassembling the equipment that has been in the acid service.

A thorough process control during the operation of the HF units can eliminate hazardous situations. The system patented by Mobil Oil [72] comprises sampling of the reactor streams and determining the content of HF, water, acid soluble oil and sulpholane using an infrared analyser. The results are compared with the stored signals to generate control signals. Unexpected developments, which could not be noticed without the control system, can now be identified so that preventive actions can be taken. Other details of the control of alkylation units were described by Ryskamp et al. [73]. Thus, the reactor isobutane/olefin ratio, temperature and throughput are the major variables in the reactor section, whereas the alkylate vapour pressure and product composition are control variables for the distillation column.

3.3.2. H_2SO_4 processes

H_2SO_4 is much less volatile than HF. Also, the potential for the formation of an aerosol is insignificant compared with the HF, though not entirely impossible. This was confirmed in the study on the release of H_2SO_4 which was initiated by a group of US refineries [74]. The objective of this study was to determine the amount of fresh and spent acids which would fall on the ground during an accidental release. The fluid was released to the atmosphere through a series of orifices, circular tubes and simulated flange gaskets. Almost 100 release tests were performed. The released acid was collected on the capture pans placed around the release vessel. The capture percentage varied between 92.5 and 100.4% with a standard deviation of 1.6. Changes in the release geometry, temperature, pressure and acid/hydrocarbon ratio did not change acid recovery by more than the experimental error.

3.4. Conversion of HF units to H_2SO_4 units and other systems

It is anticipated that growing environmental and safety concerns will force refiners to convert the alkylation units using HF to those using H_2SO_4. Previously, such a conversion required a major expenditure because only the distillation towers used in the HF alkylation could be reused. However, the ConvEx process, patented by STRATCO [75] represents a major breakthrough. In this process, the reactor, an acid settler and fractionation section from the HF alkylation can be reused, and another portion of the unit modified to suit the H_2SO_4 alkylation [76]. Another benefit from the conversion is a lower isobutane/olefin ratio in the H_2SO_4 process. This means that either less fractionation capacity will be required or feed and product rates will be increased without affecting quality of the alkylate. STRATCO has requested a third party engineering and construction company to do a cost estimate on the conversion of the existing 10 000 b/d alkylation units [77]. The cost for making the conversion was about $ 15 million. In many cases, the conversion would also allow for the capacity of the alkylation unit to expand.

It is anticipated that a change from the traditional units employing mineral acids to those using new catalysts will begin in the near future. A similar change has already taken place in the Friedel–Crafts reactions, which currently employ Lewis acids such as $AlCl_3$ and BF_3. This resulted in significantly diminishing, though not completely eliminating, the hazardous potential. Thus, $AlCl_3$ is known to react violently with the water, liberating 3 mol of HCl. As it was also pointed out by Clark et al. [78], the decomposition of the product complexes requires the addition of water which is highly exothermic, liberating large volumes of gaseous effluent (HCl) and creating an organic-contaminated aluminium rich, acidic aqueous effluent, which is increasingly expensive and difficult to handle. It appears that new alkylation catalysts will still be halogen based though in a much more maintainable form than that in HF, BF_3 and $AlCl_3$. Nevertheless, even in the distant future, the handling of alkylation catalysts may require much more attention than that of the other refinery catalysts.

3.5. Recovery of acids

The primary objective of every refiner is to recover as much HF and/or H_2SO_4 as possible on the site. This avoids costs and possible hazards associated with the storage and transportation of such materials. A number of regeneration procedures for the recovery of HF and H_2SO_4 is available.

3.5.1. Hydrofluoric acid

Efforts to recycle HF acid from alkylation are described by Coeyman and Wood [62]. According to their report, a company aims to recover almost 90% of the 17 000 metric tons annually of HF used in the alkylation unit. The recovery process employs bipolar membrane technology. In this process, potassium fluoride made by reacting the waste HF with the caustic potash is split back into the caustic potash and HF. The latter is then returned to the alkylation process.

Several regeneration procedures are found in the patent literature. The aim of regeneration is to remove the acid soluble oil from the HF and sulpholane mixture used for the alkylation. In this regard, Mobil Oil has disclosed several methods. Thus, one patent [79] comprises four steps, i.e. contacting the mixture with a sorbent to selectively remove HF, transferring the intermediate product to a separation zone, gravitational separation and withdrawal of the less-dense phase enriched acid soluble oil and more-dense phase enriched in sulpholane. In another patent disclosed by Mobil Oil [80], the spent liquid catalyst comprising HF, polymeric byproduct and sulpholane is contacted with fine solid sorbents which selectively and reversibly adsorbs the polymeric byproduct. The catalyst (mixture of HF and sulpholane) is returned to the operation. The polymeric product is desorbed from the sorbent which is then reused. Two additional patent applications are based on stripping the spent alkylation catalyst with a stripping gas in a stripping tower. In one case [81], the intermediate product containing less than 5 wt% HF is charged to a gravitational vessel to produce two partially immiscible phases, i.e. one enriched in the acid soluble oil, and the more dense phase containing sulpholane. In another method [82], the stripping is conducted to obtain an intermediate product containing less than 30 wt% HF. After cooling, this product is then separated into the sulpholane enriched stream, a conjunct polymer enriched stream and solids stream. The sulpholane enriched stream is then contacted with polar solvent to obtain a further enriched sulpholane and a raffinate streams. After stripping the solvent, pure sulpholane is dried and returned to the operation. The Mobil Oil has been making a continuous effort to improve the performance of the alkylation process with a focus on the recovery and/or regeneration of the HF [83,84].

The process claimed by Del Rossi and Melli [85] involves the HF/sulpholane alkylation in the presence of at least partially soluble metal compound. The more dense phase containing sulpholane, soluble oil, HF and the metal-containing compound is stripped to remove HF, after separating from the less dense alkylate product. The bottom from the stripper is hydrogenated to produce sulpholane enriched stream and a less dense hydrocarbon stream.

The regeneration process developed by Phillips Petroleum [86] comprises at least three separation steps. In the first step, the alkylation product is separated from the mixture of HF, sulpholane and acid soluble oil. In the next step, HF is separated from the mixture. This is followed by the separation of the oil by-product from the sulpholane. The latter is then contacted with activated carbon to remove all remaining oil by-product. In another patent [87], the sulpholane containing undesirable by-product is contacted with water to induce the formation of two immiscible phases, one containing the by-product and the other containing water and sulpholane. Two additional patents from Phillips Petroleum [88,89] use either an adsorbent or solvent extraction for removing the undesirable product from the sulpholane. In another process, the spent sulpholane is contacted with the alumina to remove the remaining HF and then with the activated carbon to remove the reaction byproduct [90]. Reversible bases such as polyvinyl pyridine, amine substituted styrene divinyl benzene copolymer and a combination of both, can be used for removing a part of the soluble oil from sulpholane prior to contacting the latter with activated carbon [91]. This yields the sulphone stream substantially free of the HF and the byproduct.

3.5.2. Sulphuric acid

The typical spent acid consists of 90 to 92% H_2SO_4, 3 to 5% water and 7% hydrocarbons. The recovery of H_2SO_4 can solve the disposal problem and even yield a reusable product. In the past, refineries were purchasing H_2SO_4 from a chemical company and the spent acid was then returned to the company for regeneration. However, if the regenerated and spent acids have to be shipped any appreciable distance, this approach becomes very expensive. The recovery of sulphur from spent acid in the refinery appears to be the most economical approach, especially if the refinery is operating a Claus sulphur plant [92].

Although the recovery appears to be an attractive option, the overall cost of the operation has to be thoroughly assessed. Thus, as it was pointed out by Ondrey and Shanley [61], the

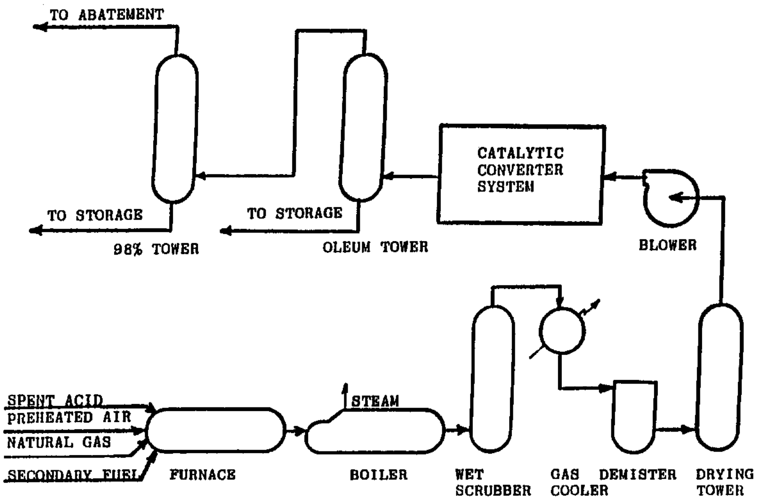

Fig. 13. Process flow schematic of regeneration of spent H_2SO_4 acid [94].

cost of the recovered acid may be 2 to 3 times that of the acid commercially available on the market. These authors show that it costs between $ 100 to 150 per metric ton to regenerate spent acid from the alkylation compared with about $ 75 per metric ton US market price. This does not include the cost of transportation in case of the off-site regeneration.

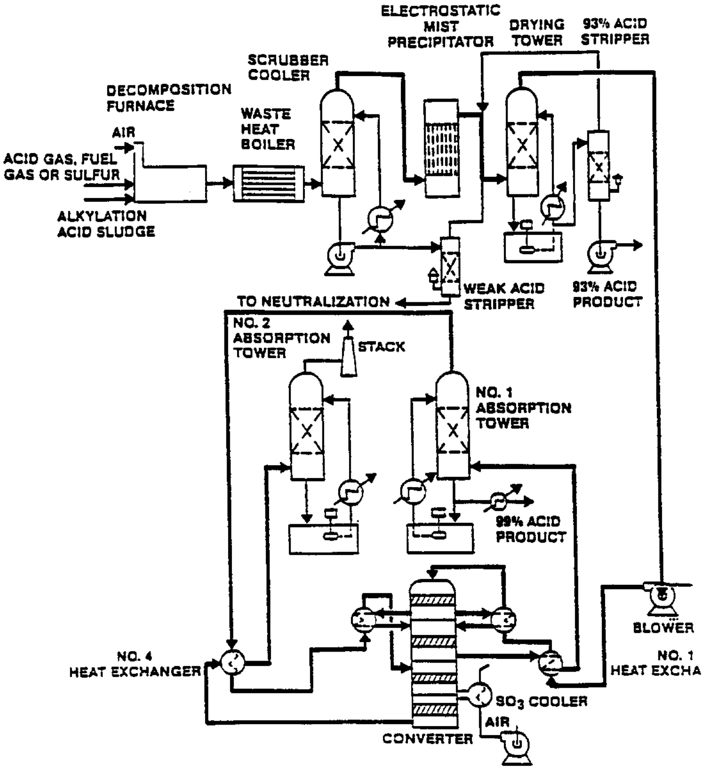

Fig. 14. Process flow schematic of alkylation sludge H_2SO_4 acid plant [92].

Sulphuric acid regeneration (SAR) can produce acid of a commercial quality. Typically, during regeneration the spent acid is incinerated by burning at about 1000°C. This step converts spent acid into SO_2 and CO_2. The clean SO_2 is then oxidized in the presence of a V_2O_5 catalyst to SO_3, which can be subsequently absorbed by H_2SO_4 to produce concentrated acid.

The regeneration process using a fuel oil instead of natural gas was described by Kogtev et al. [93]. The process is sensitive to the air/fuel ratio. Thus, an excess of air (air/fuel = 1.3) is required to achieve complete combustion and to attain a temperature of about 1000°C. Otherwise, the soot formation affected the performance. The residence time and the method of injection of H_2SO_4 into the combustion zone were other important parameters of the process.

Commercial regeneration technology can be supplied by several licensors. The schematics of the process, licensed by the Stauffer Chemical Company, is shown in Fig. 13 [94]. In this process, the spent acid is fed through the atomization nozzle into the furnace which is fired with natural gas. This yields a gas stream containing SO_2/SO_3, CO_2, N_2, O_2 and H_2O. The waste heat from the hot gas is recovered in the boiler as steam. Ash and soluble impurities (e.g. HCl) are removed in the scrubber. After cooling and drying, the gas is passing the catalytic convertor to oxidize SO_2 to SO_3. The latter is used to produce either H_2SO_4 or oleum. One information suggests that the efficiency of the recovery process can be increased by replacing the air into the atomiser by oxygen [95].

The process developed by Chemetics is a hybrid system which combines both the recovery and concentration steps [61]. In this process the acid is spray dried. This allows recovery of the inorganics in the form of dry and solid particles and a complete oxidation of the organics contaminants. At the same time, the decomposition of H_2SO_4 to SO_2 is minimized. The concentrated acid is then recovered by partial condensation.

The schematics of the process licensed by the Ralph M. Parsons Co. is shown in Fig. 14 [92]. In this process, acid sludge is sprayed into the decomposition furnace simultaneously with air. Additional heat can be supplied by burning acid gas, fuel gas, sulphur or a combination of these. The gas from the furnace must have some excess of oxygen to prevent soot formation. The gas is then cooled, freed of mist and dried in the drying tower. A stream of acid can be drawn from the drying tower circulating acid to produce 93% acid after stripping free of SO_2. After increasing the temperature and pressure of the gas leaving the drying tower, the gas enters two catalyst reactors for the conversion of SO_2 to SO_3. The latter, after being cooled is absorbed in the absorbtion tower. The 99.0 to 99.3% acid is drawn from this tower. The gas from this tower is reheated before passing another two

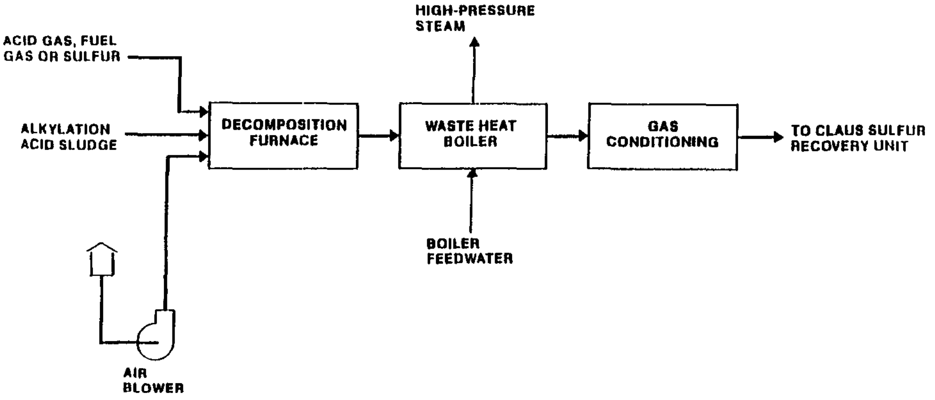

Fig. 15. Alkylation sludge decomposition for integration with sulphur recovery [92].

catalyst reactors. After cooling, the oxidized gas is absorbed in another absorbtion tower by a circulating stream of the acid. The process is flexible and can produce acid for export or only for the alkylation plant requirements. In the latter case, a small amount of the acid gas or sulphur is also burned to make up for a small amount of the acid lost during alkylation. As it is shown in Fig. 15, this process can be easily integrated with the Claus sulphur recovery unit. In this case the process employs a pressurized decomposition furnace with a separate air blower. High pressure steam can be produced by the waste heat boiler.

3.5.3. Phosphoric acid

The work published by Rakhimov et al. [96] indicates difficulties associated with regeneration of the spent phosphoric acid catalyst from polymerization. Thus, the removal of carbon by roasting resulted in the significant decrease of the activity, compared with that of the spent catalysts before roasting. Rather than to regenerate, these authors suggested to use the spent acid for preparation of the additive which could be added to the fresh catalyst. The method involved roasting the spent catalyst at about 500°C. This was followed by crushing to obtain < 1 mm particles. These particles were moisturized, pelletized and conditioned to attain about 6 wt% of moisture content. The pellets of the catalyst prepared using this method were added to the fresh catalyst. Up to 15 wt% of this catalyst could be added to the fresh catalyst load without affecting the operation.

4. Utilization of spent solid refinery catalysts

Increased costs associated with the disposal methods of spent refinery catalysts have provided incentives to reduce such wastes. This may be the best way to summarize the findings of Section 2. The disposal cost is significantly higher for the RCRA wastes. As it was indicated above, among solid spent refinery catalysts, only spent hydroprocessing catalysts are presently being classified as hazardous wastes. It is anticipated that spent FCC catalysts will also be added to the list of the RCRA wastes in the future. One way to reduce the amount of refinery wastes, such as spent catalysts, is to find some new applications. Cascading of spent catalysts, i.e. utilization in less severe operations is only a temporary solution. For catalysts containing precious metals, recovery of the metals is an obvious solution. Recovery of other metals from spent refinery catalysts is influenced by the world prices of metals which tend to fluctuate. However, if the cost of catalyst disposal will continue to rise, the utilization of spent refinery catalysts for metal recovery and other purposes may become a viable solution.

4.1. Hydroprocessing catalysts

Properties of non-regenerable hydroprocessing catalysts were described in Section 2. They always reflect the conditions to which they were subjected during the operation. They are always deposited by coke. If metals were present in the feed, a portion will deposit on the catalyst as well. Thus, besides active ingredients such as Mo, W, Co and Ni, additional metals, e.g. V, Ni, Fe, Ti and alkali metals may also be present. The original structure of the catalyst has changed as well. This may include some new compounds formed by the reaction of active metals and deposited metals, with the support or sintering of the latter caused by a prolonged exposure at operating temperatures. The combined effect of these factors is a significant loss of surface area and porosity.

The information on management of spent refinery catalysts is quite extensive. In most cases, a primary objective is to minimize or completely eliminate the cost of storage and disposal. The presence of catalytically active metals offers a number of utilization options. It appears that the metal reclamation has been attracting most of the attention. Other potential schemes may be developed in the future. The refiner is eager to supply spent hydroprocessing catalysts at no cost. In many cases, the refiner is required to offset the cost of the company involved in the reprocessing of spent catalysts. As it was indicated earlier, pressures from environmental authorities will be a driving force for finding new applications for spent catalysts.

4.1.1. Recovery of metals

Commercial technologies exist which can process low metal content catalysts [97]. However, a low metal content in spent catalysts increases processing costs. In fact, most of the companies involved in metal reclamation from spent catalysts consider this as an environmental service. Again, the influence of the world prices of metals on the commercial viability of their reclamation can be an important factor especially in the case of spent hydroprocessing catalysts. Perhaps, separation of the metal enriched part of catalyst particles or trapping (concentrating) the metals before they can contact the catalyst bed may improve the situation. In this regard, several methods can be found in the literature. For example, it was demonstrated by Clark et al. [98] that during the attrition experiments of an extrudate form of a spent catalyst, the generated fines were significantly enriched in vanadium. In another separation process, the spent catalyst, after being stripped of process oil, was fluidized by flowing air upwards to expand the catalyst bed [99]. This resulted in a segregation of particles into a high activity, upper, less contaminated fraction and a lower more contaminated fraction. The former could be returned to the operation, whereas the metal enriched fraction was suitable for metal reclamation. Macroporous solids used in guard beds protecting FCC, hydroprocessing and reforming catalysts from metal deposits and other impurities could also be attractive materials for recovery of V and Ni [100,101].

The scientific literature on metal recovery from various solids is rather extensive. In some cases, the same method can be applied to different solids including spent catalysts. In the present Section, the reference will be made only to the sources which specifically deal with the spent hydroprocessing catalysts. In case of one method, the primary objective is leaching of the metals of interest and keeping the dissolution of supports to a minimum. A special case of selective leaching is the rejuvenation of spent catalysts for possible reuse in the refinery. However, this is not easy to achieve because a small amount of the metal contaminants remains in the support, even in the case of an excellent leaching process. Then, in the case of leaching methods, the remaining support may not be acceptable for disposal without an additional treatment. The alternative treatment, avoiding the problem of solid wastes, is a total dissolution of the spent catalyst into an acid solution from which the metals are almost completely recovered by solvent extraction, leaving the support in the solution. A part of the spent catalyst can be made water soluble by a caustic treatment. The selective bioleaching of metals has been attracting attention as well. The supercritical extraction and anhydrous halogenation have also been receiving some attention.

Potential for the use of carbon supported catalysts for hydroprocessing of heavy feeds was indicated by Rankel [102]. In this case, the recovery of metals appears to be rather straightforward, i.e. the combustion of carbon would leave behind a metal concentrated solid residue.

4.1.1.1. Roasting and precipitation or solvent extraction. The methods discussed in this part of the review will include decoking, followed by roasting of the decoked catalyst in the presence of an inorganic agent. Metals will then be recovered by dissolution, followed by either precipitation or solvent extraction.

Inoue et al. [103] studied a spent Co-Mo/Al_2O_3 catalyst deposited mainly with V and Ni from the operation. The catalyst was roasted at 700°C, suspended in 63% H_2SO_4 and evaporated to dryness. Subsequently, it was dissolved in water and filtered to remove small amounts of silica. The filtrate was diluted to reach a pH of 1.2. This solution was extracted

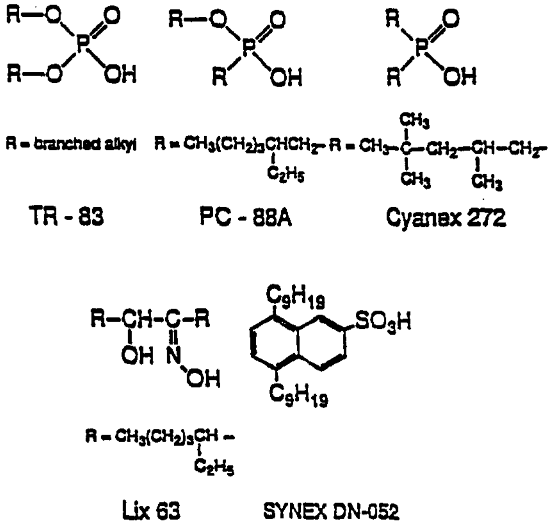

Fig. 16. Some commercial solvent extraction agents [103].

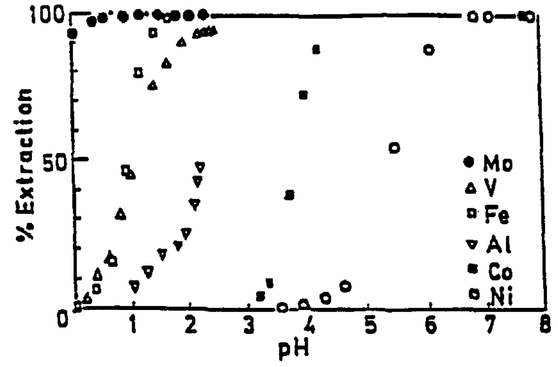

Fig. 17. Extraction of metals with 20 vol% Cyanex 272 in EXXSOL D 80 [103].

by a series of commercial extracting agents, some of which are shown in Fig. 16. The Cyanex 272 in EXXSOL D 80 as diluent was efficient for selective removal of Mo. Thus, as the results in Table 14 show, an excellent separation of Mo from the V, Co, Ni, Al and Fe was achieved at pH approaching zero. The stripping of Mo from the solvent was then achieved using an aqueous ammonia solution. A good phase separation was achieved at pH between 8.0 and 8.4. After Mo was separated, the pH of the scrub solution was increased to about 1.5 by adding $Ca(OH)_2$ powder. At this pH, V was separated using Cyanex 272 as the extractant. Almost all V could be stripped from the solvent using aqueous ammonia solution. As the results in Fig. 17 show, the separation of Co and Ni from Al can be achieved but the procedure may be too costly. This problem was overcome by the method developed by the AMAX Inc [104]. In this method, the extractant is a mixture of LIX 63 and SYNEX DN-052 in the EXXSOL D80. The separation results obtained by mixtures of these extractants are shown in Fig. 18. It is quite evident that the final separation of Ni and Co from Al in the raffinate, left after the separation of Mo and V, can be achieved. Inoue et al. [105] expanded their study to include commercial reagents such as TR-83, PC-88A and PIA-8. The performance of PIA-8 was similar as that of CYANEX 272. Thus, Mo can be nearly completely extracted at

Table 14
Extraction of metals from aqueous solution [a] with 40 vol% Cyanex in EXXSOL D80 at 40°C [103]

pH	Extraction (%)					
	Mo	V	Fe	Al	Co	Ni
0.03	99.5	9.8	3.45	0.15	0	0
0.21	99.6	16.1	3.45	0.22	0	0
0.35	99.7	22.5	16.7	1.44	0	0
0.51	99.7	32.2	33.3	0.27	0	0
1.00	99.8	80.4	84.4	1.05	0	0
1.51	99.7	92.5	100	1.89	0	0

[a] Average content of metals in the solution before the extraction (g/l): Mo = 2.70; V = 0.75; Fe = 0.030; Al = 13.50; Co = 1.00; Ni = 0.17.

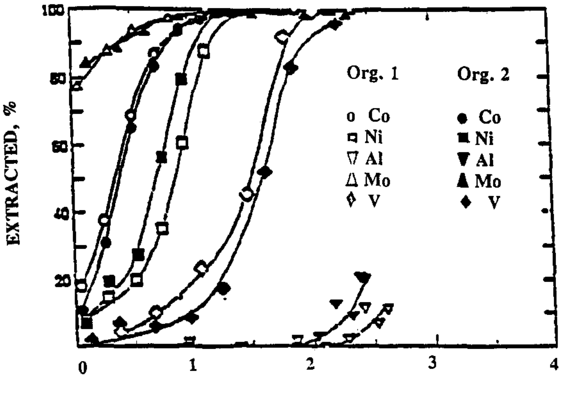

Fig. 18. Effect of pH on synergistic extraction with SYNEX DN-052/LIX 63 mixture [103].

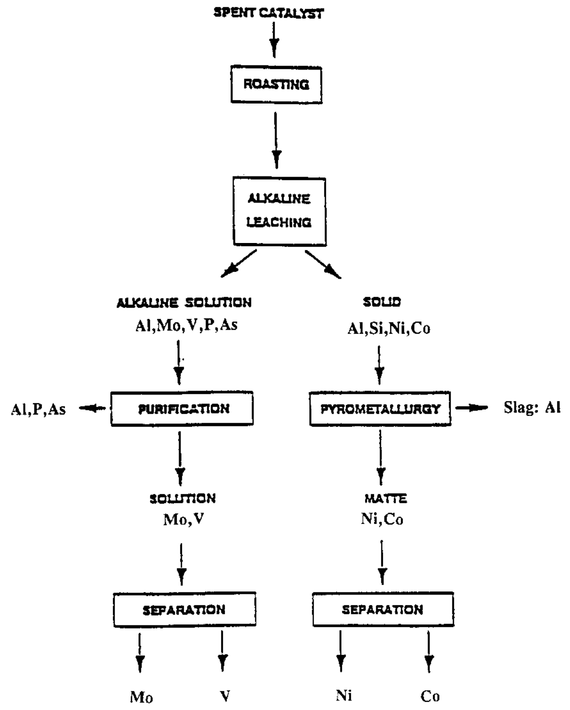

Fig. 19. Flowsheet of metal extraction from leach liquor [105].

a pH approaching zero. V, Fe and small amounts of Al coextracted with Mo into the solvent phase were scrubbed using different concentrations of H_2SO_4 before Mo was recovered. More than 90% of Mo was separated from the solution by stripping with 5 to 7% ammonia. V can be further recovered from the scrub solution containing Fe and a small amount of Al with PIA-8 or CYANEX 272 after adjusting the pH to about 1.5 by the addition of $Ca(OH)_2$. Subsequently, V can be recovered by stripping with the aid of 6% aqueous ammonia. After recovery of the Mo and V, the final separation of Co and Ni from the large amount of Al in the sulphate leach was achieved by the mixtures of LIX 63 and CYANEX 272 or PIA-8. The separation of Ni from Co can be easily achieved using conventional methods described by Ritcey [106]. This involves solvent extraction using long chain alkylamines. The Al, as the last metal left in the original solution, can be also isolated in a pure form by precipitation. The exhaustive studies by Inoue et al. [103,105] resulted in the flowsheet for recovery of metals from spent hydroprocessing catalysts shown in Fig. 19.

The invention patented by van Deelen [107] involves roasting the spent catalyst in an oxidizing environment at 1000 to 1200°C for 0.5 to 3 h in order to convert gamma Al_2O_3 to α-Al_2O_3, but preventing sintering of the latter. Subsequently, the metals such as Mo, W, Ni, Co and V are solubilized from the roast using an acid medium at pH of 1–2. The final recovery of metals from the solution can be accomplished by solvent extraction.

In the study published by Toda [108], sodium containing agents such as Na_2CO_3, NaOH and Na_2SO_4 were roasted with a spent HDS catalyst at 1123 K. The roasted products were dissolved in hot water. The best results were obtained with Na_2CO_3. The other agents enhanced dissolution of Al_2O_3, which was unwelcome. The extraction of Mo and V approached 96%. However, incomplete oxidation of the catalyst during roasting affected the extraction. A weak base ion exchange resin was used for separation of Mo(VI) and V(V) from the solution. The salting-out method of ammonium vanadate using NH_4Cl and an acid precipitation method to recover molybdic acid, using HCl were also examined. Both methods were efficient for recovery of Mo and V.

Biswas et al. [109] used NaCl + H_2O vapour to roast the decoked Co-Mo/Al_2O_3 catalyst used in a heavy oil upgrading. After 2 h roasting at 850°C, the catalyst was leached with water at 100°C. The results in Table 15 show that more than 80% of the V and Mo could be leached out at 100°C. Most of the V was precipitated from the leachate using $(NH_4)_2SO_4$ at pH

Table 15
Percentage of material dissolved on leaching of roasted catalyst [109]

Leaching temp. (°C)	V	Mo	Al	Co	Ni
100	81.85	81.78	0.25	0.05	0.31
80	78.52	73.90	0.25	0.04	0.18
52	76.64	65.10	0.25	0.09	0.12
35	69.20	58.05	0.22	0.08	0.10

8.6. The Mo was separated from the remaining V in 0.05 M sulphite ion medium by extracting with tri-*n*-octylamine, stripping with NH_4OH and precipitating by the acidification of the stripped solution.

A Co-Mo/Al_2O_3 catalysts, crushed to minus 100 mesh was used by Ference and Sibenik [110] for the recovery of Mo and Co. The catalyst was first decoked in an oven and subsequently roasted with the Na_2CO_3 in the air at 750°C to convert MoO_3 to Na_2MoO_4. The water leaching of the product at 100°C resulted in the dissolution of Na_2MoO_4. The filtration of the solution resulted in a good separation of Co-Al_2O_3 which remained in the cake. The filtrate was treated with either $CaCl_2$ or CaO to produce $CaMoO_4$ precipitate. The laboratory scale system used by these authors could achieve Mo recoveries between 90 and 95% with little Co contamination.

The commercial process developed and used by EURECAT also employs a caustic treatment (roasting) of the decoked catalyst with soda [44]. The schematics of this process are shown in Fig. 20. The obtained solid is then leached with hot water to remove Mo, W, V, As and P. The Ni, Co, Fe and most of the alumina are not leached out and remain in the cake after filtration. The leaching efficiency is controlled by the parameters such as pH, concentration, liquid/solid ratio, potential redox, residence time, etc. The process is continuous with a countercurrent percolation, using 12 tanks in a series. The filtrate contains Na salts of molybdate and/or tungstate, vanadate, and impurities such as arsenate and phosphate. The filtrate is purified to remove arsenate, phosphate and small amount of aluminate before the extraction of Mo and/or W and V. These impurities are removed by precipitation. The ion exchange

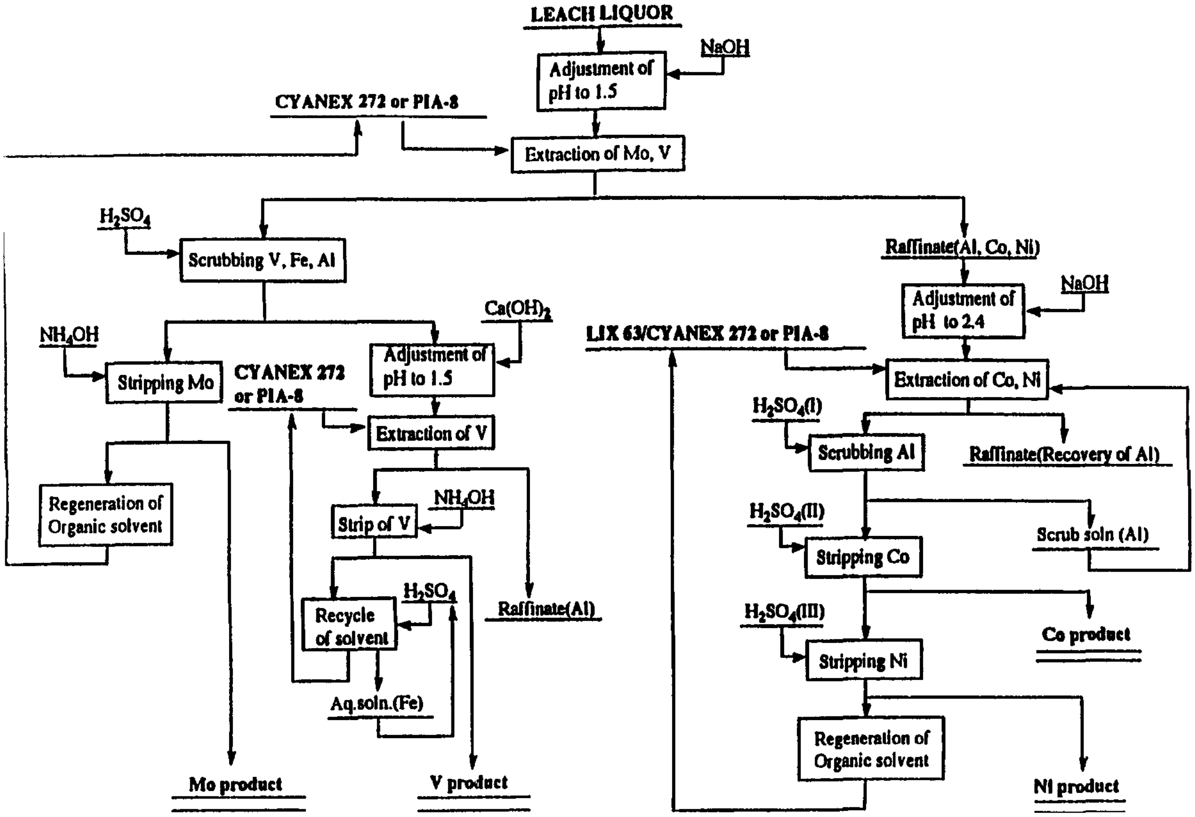

Fig. 20. Flowsheet of EUROCAT recycling process [44].

resins are used to separate Mo and/or W from V. The nature of these resins appears to be a proprietary. The filtrate cake containing between 2 and 4% of Ni and/or Co is sold to a company involved in Ni and Co production.

The CRI-MET two stage process (Fig. 21) was described in detail by Kunzelman et al. [53]. In this process, the spent catalyst is pulverized and slurried before being pumped into an autoclave where the Mo and V are solubilized, sulphur converted to sulphates and the coke partially oxidized by wet air oxidation. Further processing of the filtrate yields MoS_3 and V_2O_5 which are both marketable products. In the second stage, the alumina is solubilized as Na aluminate together with the remaining Mo and V. The Na aluminate is recovered from the liquor as very pure $Al(OH)_3$. After the precipitation of $Al(OH)_3$, the remaining liquid is pumped back to the second stage of autoclave to solubilize more alumina. The Ni and/or Co loaded cake is sold to smelting companies.

Mo can be recovered in the form of molybdic acid using a process based on treating the spent catalyst with 1 to 3 parts of H_2SO_4 per 1 part of the spent catalyst [111]. The process employs a sulphide atmosphere between 20 and 200°C and pressure of 1 to 35 atmospheres. This is followed by the separation of $Al_2(SO_4)_3$ from the sulphide precipitate which was finally oxidized as a sulphide slurry.

Mo dispersed in a slurry may be an efficient catalyst for coal liquefaction. However, a suitable method must be found for Mo recovery from liquefaction residues. Ference and Sibenik [110] used a partial oxidation of the residue as the first step, followed by the fusion of the ash. After cooling, the ash was ground to minus 100 mesh and mixed with Na_2CO_3. The mixture was then roasted at 700°C. This was followed

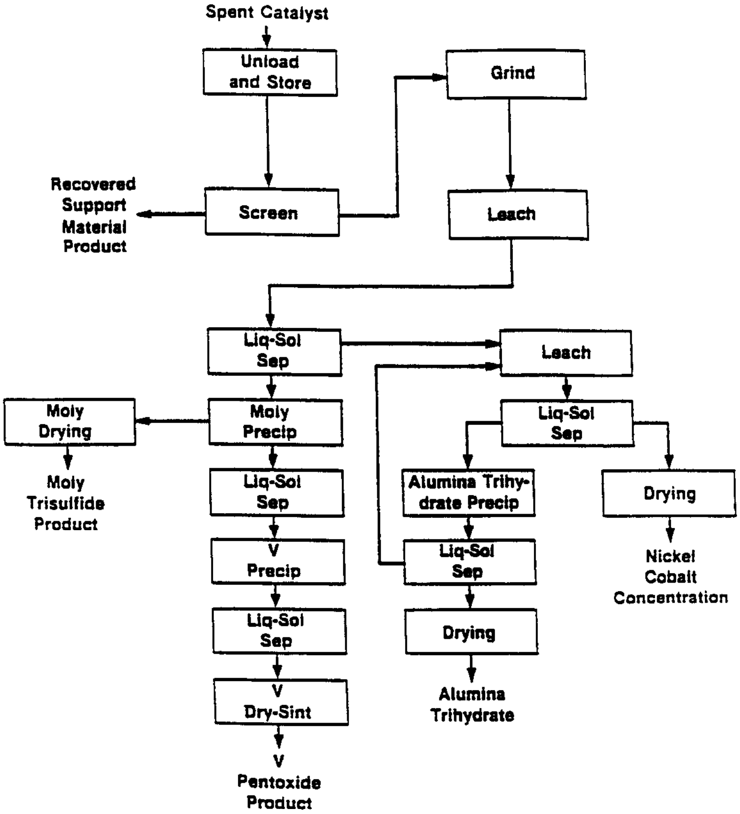

Fig. 21. Flowsheet of CRI-MET recycling process [53].

by the dissolution of Na_2MoO_4 in hot water. The filtrate was mixed with the ammonia before adjusting the pH to about 2 by adding H_2SO_4 to precipitate ammonium polymolybdate. The work published by Krastman et al. [112] explains the need for adding Na_2CO_3 to the ash before roasting. Thus, in the absence of Na-containing compounds, Mo combined with the Ca from ash to give $CaMoO_4$. This compound is unreactive with ammonia and as such inhibits Mo recovery. Roasting in the presence of Na-containing compounds (e.g. NaOH and Na_2CO_3) gives soluble molybdate, which is suitable for recovery from the solution by precipitation.

4.1.1.2. Leaching. In the case of leaching, the primary objective is to selectively leach out metals of interest from the support while leaving most of the support intact. In this case, decoking is the only treatment to which the spent catalyst is being subjected. The metals can be isolated from the spent catalysts by leaching, using solutions of the organic and inorganic agents or combinations of both. The former are based on organic compounds which form water soluble complexes with the metals. The inorganic solutions are usually of ammoniacal as well as caustic and acidic natures. Among the latter, concentrated H_2SO_4 and solutions of NaOH have been used. Mixtures of salts and acids are also being used.

Organic agents and mixed agents. In this Section, the primary focus will be on leaching of metals using aqueous solutions of organic agents and various mixtures of organic and inorganic agents.

The pioneering work on leaching of the metals from spent hydroprocessing catalysts using aqueous solutions of the organic agents was published by Beuther and Flinn [113]. The agents included eight organic acids in addition to some amines, aldehydes and ketones. The experimental set-up was based on the up-flow percolation of the solution through the fixed bed of the catalyst. Some results from this study are shown in Table 16. The 1.0 wt% aqueous solution of these agents were used. The leaching experiments were performed at the ambient temperature and pressure, using 15 g of catalyst and 1.0 l of the solution which was recycled for 4 h at the rate of 0.5 l/h. The leaching efficiency increased with increasing temperature.

The results shown in Fig. 22 suggest that for glyoxylic acid, the optimal concentration is somewhere between 1 and 2 wt% [114]. Similar trends were observed for tartaric, citric, lactic and glycolic acids. These results were obtained by putting 2.5 g of catalyst in contact with 100

Table 16
Organic agents [a] used for leaching of spent catalysts [113]

Agent	Metal content in catalyst (wt%)				Leaching efficiency (%)			
	V	Co	Ni	Mo	V	Co	Ni	Mo
Oxalic acid	1.0	0.4	0.4	3.1	47	60	56	59
Lactic acid	1.1	0.5	0.5	4.8	42	50	44	37
Citric acid	1.0	0.8	0.5	6.6	47	20	44	13
Glycolic acid	1.2	0.8	0.7	8.0	37	20	22	5
Phtalic acid	1.2	0.5	0.7	6.5	37	50	22	14
Malonic acid	1.1	0.6	0.6	5.6	42	40	33	26
Succinic acid	1.3	0.8	0.8	6.9	32	20	11	9
Salicylic acid	1.2	1.1	0.7	5.4	37	10	22	29
Tartaric acid	1.2	0.4	0.5	3.6	37	60	44	53
Salicylaldehyde	1.3	0.9	0.8	5.4	32	10	11	29
Aminophenol	1.4	1.2	0.8	5.4	24	20	11	29
Ethylenediamine	1.2	1.1	0.7	5.2	38	10	22	32
Acetylacetone	1.4	0.8	0.8	4.9	29	20	11	35

[a] Washing conditions: 1.0 wt% aqueous solutions; ambient temperature; 4 h; 1.0 l of solution recycled over 15 g of catalyst at 0.5 l/h.

ml of the solution at 50°C for 1 h in a flask which was immersed in an ultrasonic bath. The decoking of the catalyst significantly increased the leaching rate, whereas crushing the catalyst had little effect. Once the metals are in the solution, their separation may be achieved by an extraction such as the one described earlier.

The original work of Flinn and Beuther [113] has been advanced by Stanislaus et al. [115,116]. Primary objective of these authors was the catalyst rejuvenation for reuse in the refinery. Therefore, their aim was to develop a method which can selectively remove contaminant metals, such as V and Ni, leaving active metals intact. For this purpose, they investigated acids such as oxalic, malonic and acetic alone, and in the mixture with inorganic salts such as aluminium nitrate, aluminium sulphate and ammonium nitrate. The spent catalyst was Co-Mo/Al_2O_3 contaminated with the coke, as well as V and Ni. Leaching experiments were conducted in a fixed bed. The reagent was pumped from the bottom, collected in a vessel and recirculated through the catalyst bed. For the acids alone, the following order of the leaching efficiency was established: oxalic > malonic > acetic. Among inorganic reagents, the aluminium nitrate was the most efficient. Its effect on the leaching of V and Ni is shown in Figs. 23 and 24, respectively. The beneficial effect on leaching was attributed to the capability of the aluminium nitrate to oxidize the catalyst. Thus, little oxidation could be achieved by the other inorganic reagents. Stanislaus et al. [115] also made an effort to propose the mechanism of the leaching. This mechanism considers four important steps which occur during leaching, i.e. diffusion of the leaching agent to the solid–liquid interface, reaction between the solid and reagent to form a product, dissolution of the product in the reagent, and diffusion of the product from the reagent. These authors also studied the kinetics of leaching, namely the effect of acid concentration and temperature on the rate of

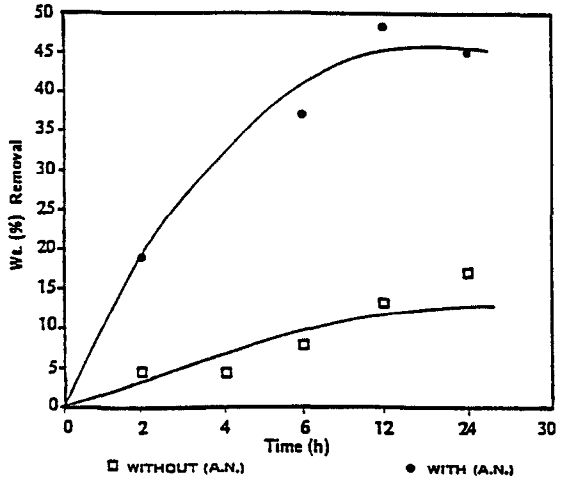

Fig. 23. Effect of adding aluminium nitrate to oxalic acid on vanadium removal [115] (acid concentration = 0.66 M; aluminium nitrate concentration = 1 M).

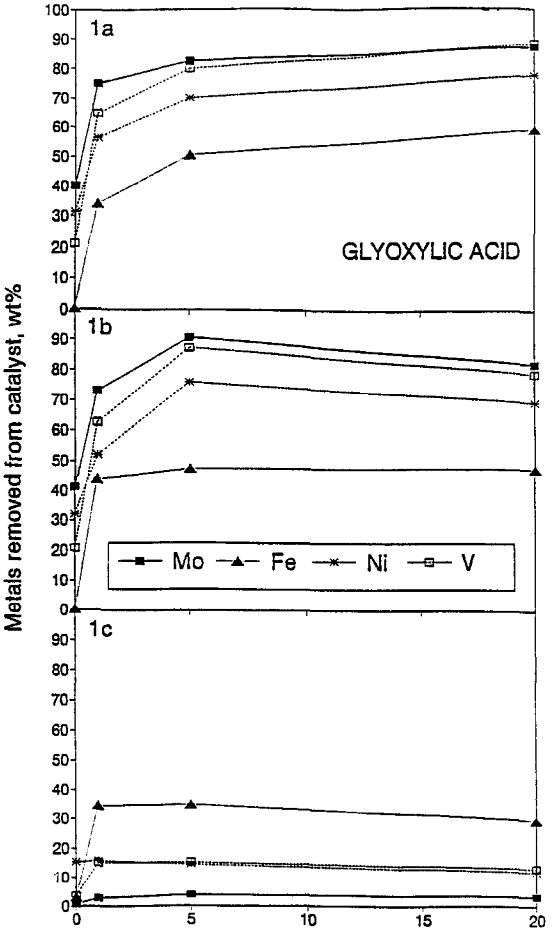

Fig. 22. Effect of glyoxylic acid concentration on leaching of metals [114].

leaching. For this purpose they used oxalic acid. The temperature increase from 25 to 75°C increased the rate significantly, whereas the concentration change from 0.33 to 1.0 M had little effect. For the coked catalyst, the mass transfer through the layer of the coke was rate determining. This layer slowed down the leaching process.

The ferric nitrate–organic acids (oxalic and tartaric) mixed reagents were used by Marafi et al. [117] for leaching a Co-Mo/Al_2O_3 catalyst deactivated by coke and deposits of V and Ni. As the results in Fig. 25 show, the leaching efficiency was significantly enhanced by the addition of ferric nitrate to tartaric acid. The beneficial effects were attributed to the synergy of oxidizing and complexing reactions. The properties of the leached catalysts, such as activity, surface area and pore volume, also improved.

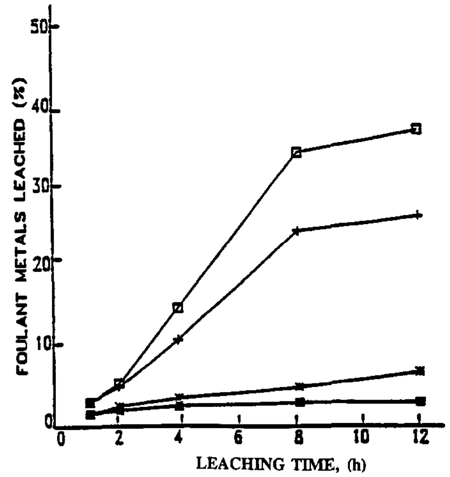

Fig. 25. Effect of adding ferric nitrate to tartaric acid on removal of vanadium and nickel [117]: □, V leached with 0.66 M acid; +, V leached with 0.66 M acid + 0.66 M ferric nitrate; *, Ni leached with 0.66 M acid; ■, Ni leached with 0.66 M acid + 0.66 M ferric nitrate.

The same organic acids which were studied by Flinn and Beuther [113] were reexamined by Reda [118] in the absence and the presence of the Fe(II)/Fe(III) redox couple. The leaching agents contained 1% of the acid and 10^{-2} M of the redox couple. In the presence of the redox couple, leaching of Mo was significantly decreased compared with that of the V. The most pronounced difference was observed in the case of oxalic acid, for which leaching of Mo decreased by a factor of 7, whereas that of V decreased by only about 30%. For oxalic, tartaric, citric and acetic acids, the Ni removal was unaffected by the redox couple. Only in the case of lactic acid, the Ni removal decreased by a factor of 2.

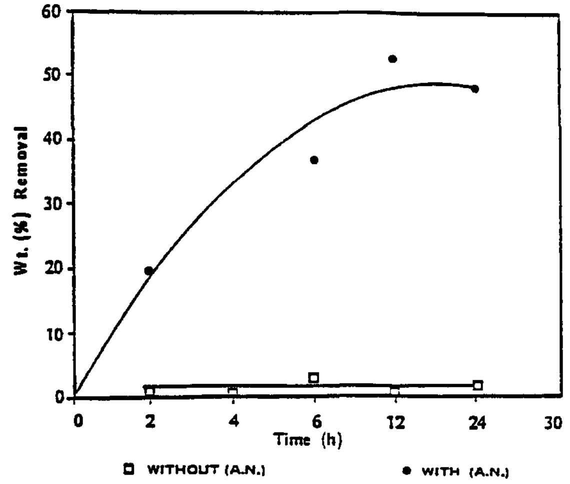

Fig. 24. Effect of adding aluminium nitrate to oxalic acid on nickel removal at 25°C [115] (acid concentration = 0.66 M; aluminium nitrate concentration = 1 M).

Recognizing the effect of partial oxidation of the spent catalyst, Stanislaus et al. [119,120] compared the leaching of decoked (oxidic) and coked (sulphidic) catalysts. The former was prepared by a controlled oxidation of the spent catalyst in a fixed bed reactor. Oxalic acid alone and the mixture of oxalic acid + H_2O_2 were used as leaching agents. Effect of decoking and the presence of H_2O_2 on Ni removal is shown in Table 17. The V removal was influenced in a similar manner. However, as the results in Fig.

Table 17
Effect of H_2O_2 on leaching of Ni [119]

	Amount of Ni leached (wt%)	
	Coked catalyst	Decoked catalyst
Oxalic acid	3.6	60.3
Oxalic acid + H_2O_2	47.0	76.5

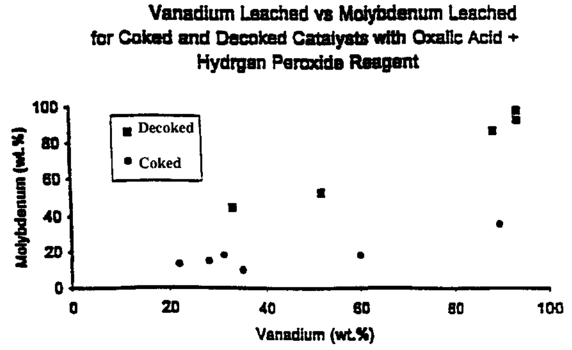

Fig. 26. Effect of decoking on leaching of molybdenum and vanadium using oxalic acid + hydrogen peroxide solution [119].

26 show, decoking increased Mo removal which was undesirable.

The DMSO–SO_2 solvent was used for selective leaching of Mo from a spent Co-Mo/Al_2O_3 catalyst by Raisoni and Dixit [121]. The work was performed in a stirring reactor. Effects of stirring speed, SO_2 concentration, particle size and temperature were established. Mo was selectively leached out as Mo disulphate, whereas Co remained unleached. The leaching efficiency increased with increasing temperature and stirring speed, and decreasing particle size.

Inorganic agents. The extrudates of spent-decoked CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts were leached in the two stage process by Angelidis et al. [122]. In the first stage, up to 97% of Mo was recovered by leaching using NaOH solution. The simultaneous leaching of Al, Co and Ni was minimized by adjusting the NaOH concentration. Up to 92% recovery of Co and Ni was achieved in the second stage using H_2SO_4.

The METREX Process described by Jocker [47] uses H_2SO_4 as leaching agent. Prior to the leaching, the spent catalyst is decoked in a furnace. The metal oxides are then dissolved in the acid. Alumina and/or silica are separated by means of decanting, washing and filtration from the liquor containing metals. The metals are isolated from the liquor by solvent extraction carried out in several stages, i.e. the first Mo, followed by V, Co and Ni. The alumina residue is used for production of the refractories. MoO_3 is sold to steel industry whereas ammonium molybdate and vanadate are sold as intermediate chemicals. Co and Ni sulphates are used for production of Ni and Co powders.

Siemens et al. [123] also used H_2SO_4 in addition to the mixture of $NH_4OH + (NH_4)_2SO_4$ and an NaOH solution to leach three spent catalysts. The results of these tests are shown in Table 18. The mixture of $NH_4OH + (NH_4)_2SO_4$ was the best for separation of the metals from the alumina support. This work was further expanded by Jong et al. [124]. Thus, the spent catalysts after being leached with an NaOH solution to solubilize Mo and/or W, were leached with H_2SO_4 to solubilize Ni and/or Co. Mo was then recovered from the caustic leach solution by solvent extraction followed by precipitation with the $CaCl_2$ to give $CaMoO_4$. The W was recovered by evaporation of the ammoniacal strip solution to yield $(NH_4)_{10}W_{12}O_{41}$. The acid leach was treated with NH_4OH–$(NH_4)_2SO_4$ mixture to precipitate Al and other metal impurities. At about pH 10, Ni was recovered by solvent extraction. At about pH 5, Co and Ni were recovered by precipitation with Na_2S.

Hildebrandt et al. [125] showed that a high level of selective leaching of the contaminant

Table 18
Metal recovery by leaching using inorganic agents [123]

Spent catalyst	Method	Extraction (wt%)			
		Ni	Mo	Al	
Ni-Mo	leaching by				
	NH_4OH-$(NH_4)_2SO_4$	90	89	0.1	
	H_2SO_4	98	93	96	
	NaOH	0.08	96	34	
Ni-W	Ni	Mo	Al		
	NH_4OH-$(NH_4)_2SO_4$	44	64	0.04	
	H_2SO_4	94	28	76	
	NaOH	0.03	91	25	
Co-Mo		Co	Mo	Al	As
	NH_4OH-$(NH_4)_2SO_4$	29	28	0.06	34
	H_2SO_4	59	5	45	60
	NaOH	0.03	31	3	54

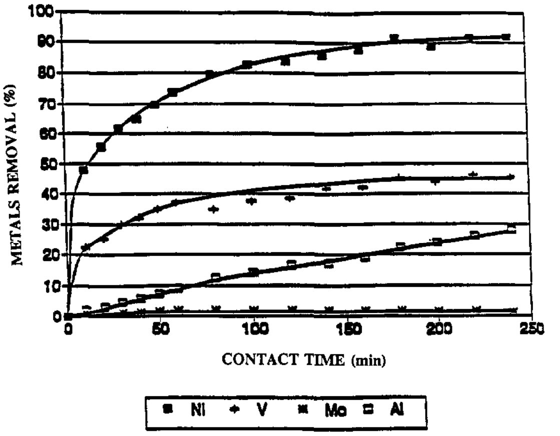

Fig. 27. Metals removal with 15 wt% H_2SO_4 (Ni removal includes contaminant Ni only) [125].

metals such as V and Ni from spent Ni-Mo/Al_2O_3 catalysts could be achieved by properly adjusting concentration of H_2SO_4. For example, the results in Fig. 27 show that for 15% H_2SO_4, the rate of removal of the contaminant V and Ni was significantly greater than that of Mo and Al. De-oiling of the spent catalyst proceeded the leaching step. After removing the contaminant metals, the catalyst was decoked by oxidative burnoff. Apparently, a good selectivity for leaching the contaminant metals could not be achieved for the catalyst which was decoked prior to the leaching. Although the primary objective of their work was catalyst rejuvenation for reuse, the results are relevant for the metal recovery as well.

The studies published by Olazabal et al. [126–128] focused on the recovery of metals from the Spanish spent hydroprocessing catalysts. The authors used a computer simulation to select optimal extraction conditions, followed by experimental verification. The catalysts were leached by alkaline solutions to remove Mo and V, followed by leaching with sulphuric acid to remove Co and Ni. The Al impurity removed during the alkaline leach (with Mo and V) was removed from the liquor by extraction using the organic phase containing 10% LIX 26 and 10% *n*-octanol in hexane after adjusting pH to 7.3 [126]. The V can then be separated from Mo using a quaternary ammonium salt (Aliquat 336)/toluene mixture in pH range of 8 to 9 [127]. The separation of Al, Co and Ni from the acidic solution can be achieved by selective extraction as a function of pH using CYANEX 272/hexane mixture [128]. Al is first removed at pH equal to 4.7. Co is then removed in two extraction steps at pH values of 6.3 and 5.0. The purified Ni in the final aqueous solution can be recovered by electrowinning.

The mixture of $FeCl_3 + HCl$ was used to rejuvenate spent Co-Mo/Al_2O_3 catalyst for possible reuse in the refinery [129]. The decoked catalyst in the oxidic and sulphided form was investigated. The sulphiding increased selectivity for V and Ni removal and reduced the removal of Co, Mo and Al. Some results from this work are shown in Fig. 28. In this case, the leaching was performed at 100°C. The flowsheet for the extraction of metals from spent Ni-W/Al_2O_3 catalyst developed by Kelebek and Distin [130] is shown in Fig. 29. In this process, the Ni extraction exceeded 95%. When the catalyst was preoxidized, this level of extraction was achieved in a single stage. The extraction temperature should not exceed 95°C. Otherwise, the solid tungstic acid was formed

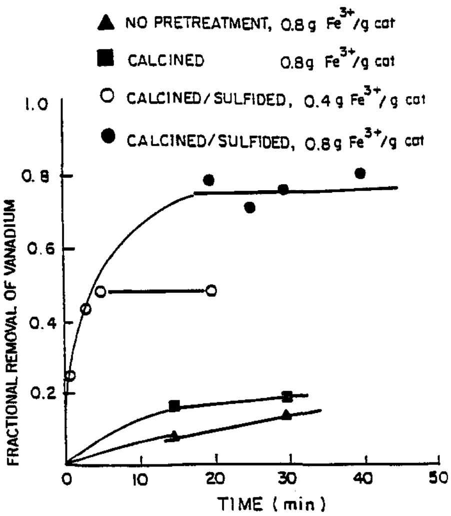

Fig. 28. Effect of pretreatment on vanadium extraction efficiency [129].

on the surface. The preoxidation temperature should not exceed 300°C to avoid nickel–tungstate formation. Coextraction of W and Al amounted to about 30 and 50%, respectively. Remaining W could be extracted from the acid leach residue using ammonia or NaOH leach.

The solution of potassium-containing compounds such as hydroxide, carbonate and acetate were compared for leaching of V from a spent catalyst [131]. The V leaching efficiency was superior for the hydroxide compared with the other compounds. Nadirov and Petrashov [132] have shown that leaching of V from the spent catalyst using a solution of NaOH can be enhanced by applying an electric current. As the results in Fig. 30 show, when the current was applied, the leaching efficiency increased by about 15%. The leaching was most extensive in the initial stage, i.e. during the first 30 min, almost 80% and more than 90% of V was leached out without and with an electric current being applied, respectively.

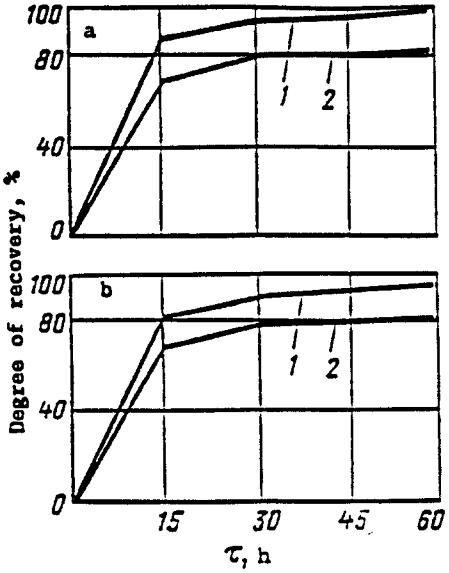

Fig. 30. Effect of leaching time on degree of vanadium recovery from spent catalyst [132]: (a) in 1 M NaOH solution, (b) in 5 M NaOH solution, (1) with application of electric current, (2) without application of electric current.

The spent catalyst, after being decoked at 360°C in air and subsequently crushed, was leached using a 10% aqueous solution of $(NH_4)_2CO_3$ [133]. Using the catalyst/solution ratio of 50 g/l at 80°C, about 45%, 77% and 65% recovery of Ni, Mo and V, respectively was achieved. The V was separated as the ammonium vanadate precipitate by cooling the liquor to room temperature. Ni and Mo were recovered by a solvent extraction. In a similar work, Mutsukawa [134] used aqueous solutions of NH_4OH, $(NH_4)_2CO_3$, NaOH and Na_2CO_3 alone or in the mixture with hydrogen peroxide for leaching Mo and V. The best metal recovery was achieved using Na_2CO_3 in the presence of hydrogen peroxide at 60°C using the catalyst/solution ratio of 20 g/l. The methods for separation of V from Mo were also examined and a flowsheet of a process was proposed.

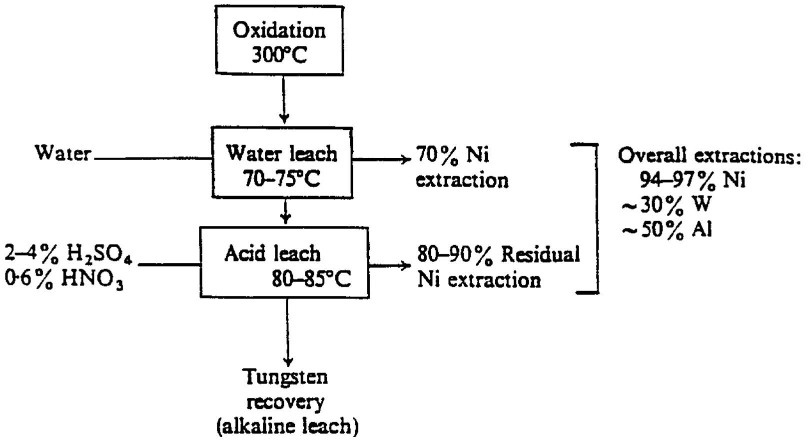

Fig. 29. Simplified flowsheet for nickel extraction from NiWAl spent catalyst [130].

Rokukawa [135] used solutions of H_2O_2 for leaching Mo, V, Ni and Co from spent HDS catalysts. The H_2O_2 concentration varied between 0.5 and 6%. In this concentration range, the leaching efficiency increased with concentration and achieved almost 99% for Mo, 85% for V, 95% for Ni, 98% for Co and less than 7% for Al. Once in solution, the metals were recovered by a series of precipitation steps [136]. Thus, Ni and/or Co were precipitated as their hydroxides by adjusting the pH of the solution to 13 with NaOH. The V deposited as NH_4VO_3 by adding NH_4Cl with a pH adjusting to 8 with HCl. Mo was precipitated by adding $CaCl_2$ and adjusting the pH of the solution to 5. Each separated component could be further purified by redissolution, recrystallization, solvent extraction, ion exchange resin or electrolysis.

A number of studies on recovery of metals from various solutions have appeared in literature. It is felt appropriate to mention these studies, although details of the spent catalyst dissolution and/or leaching are not given. For example, Nishizawa et al. [137] have shown that a selective adsorption of Mo and V from solution can be achieved using polystyrene resins. The resins were cross-linked with bis-(2-hydroxyethyl) amino, bis-(carboxymethyl) amino and bis-(phosphonomethyl) amino groups. In this technique, a chelating resin was swollen with the water and poured onto a glass column, which was conditioned with the dilute HCl in advance. A solution containing Mo and V was passed through the column and the effluent analyzed. The best results for effective column separation were achieved with the resin cross-linked with bis-(2-hydroxyethyl) amino group. Sato et al. [138] used 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester dissolved in *n*-heptane for extracting Mo from a solution. In the same study, a reference was made to numerous studies using various extractants, such as high molecular weight alkylamines (tri-*n*-octylamine and tri-*n*-octylmethyl ammonium chloride), di-2-ethylhexyl phosphoric acid, tri-*n*-butyl phosphate, sulphoxides, B-hydroxy oximes and 2-ethanol trifluoro acetone. The most recent study published by Hirai et al. [139] focused on bis (2-ethylhexyl) phosphoric acid as agents for the extraction of Mo and V from a weak acidic sulphate and chloride media. It is believed that the list of such extractants will continue to grow. Once in the solution, V can be separated from Mo by photoreductive stripping [140,141]. In this case, formic acid was more efficient reducing agent than isopropyl formate. A halogen lamp and a mercury lamp were used for the irradiation.

Leaching by supercritical fluids. In the supercritical phase region, fluids have very high liquid-like densities which result in a high capacity for solutes. In addition, they exhibit gas-like transport properties. Their viscosity is almost as low as that of gases and the diffusibility is at least one order of magnitude higher than that of liquids. The combination of these properties makes the supercritical liquids an ideal class of solvents for leaching metals from microporous solids.

McPartland and Bautista [142] described in details the experimental system suitable for supercritical leaching. They compared leaching efficiency of Co from the spent $Co-Mo/Al_2O_3$ catalyst using a solution of supercritical and subcritical aqueous ammonia. The results of these experiments are summarized in Table 19. It is evident that leaching of Co under supercritical conditions was enhanced when compared with leaching at supercritical pressure-elevated

Table 19
Efficiency of Co extraction from $Co-Mo/Al_2O_3$ catalyst using solution of supercritical (SC) and subcritical aqueous ammonia [142]

Mol% NH_3	Low-press. Low-temp.	SC press. Low-temp.	SC press. Elevated temp.	SC press. SC temp.
5	0	0	0	0
10	26.7	25.6	5.6	29.3
15	31.6	39.1	24.1	35.0
20	36.1	39.5	35.0	44.3
25	32.3	40.2	35.0	50.0
30	48.9	45.3	39.1	51.1

temperature low pressure-low temperatures and supercritical pressure-low temperature conditions by about 14.2, 6.8 and 4.0%, respectively. The higher leaching efficiency under supercritical conditions was achieved with less amounts of solvents compared with the other conditions.

Bioleaching. Blaustein et al. [143,144] applied a bioleaching technique for the Mo recovery from a coal liquefaction residue containing about 2 wt% of Mo. The approach was based on the ability of some bacteria to oxidatively solubilize MoS_2. Thus, the bacteria *Thiobacillus* (*T*) *ferrooxidans* can enzymatically oxidize Mo(V) to Mo(VI). The *T. ferrooxidans* strain 13661 and *L. ferrooxidans* were used as organisms. All growth and bioleaching experiments were conducted in an autoclave at 28 to 30°C with shaking at 170 to 200 rpm for about six weeks. The CO_2 present in the ambient air was used as the carbon source for the bacteria. The schematics of the process are shown in Fig. 31. The Mo was concentrated in the leachate B, acid-extract liquid D and acid-extracted residue E. The amount of solubilized Mo increased with decreasing particle size of the solid residue.

The US Department of Energy has initiated several projects on microbial recovery of metals from spent hydroprocessing catalysts. In one study, the NiMo catalyst used for coal liquefaction was treated with microorganisms such as *T. ferrooxidans*, denitrifiers and Sulfolobus [145]. It was observed that the catalysts containing Mo and W required special attention. Thus, only microorganisms which are tolerant to these metals can be used efficiently. The *T. ferrooxidans* were good for releasing Ni from the catalyst but toxic effect of Mo on the bacteria resulted in the use of a large volume of liquids and long contact times. The efficient leaching of both Ni and Mo was achieved by using the heterotrophic denitrifying bacteria. In a similar study, thermophilic cultures such as *Bacillus stearothermophilus* and *Metallosphera sedula* were grown by Sandbeck and Joffe at 60°C [146,147]. Mo release from spent catalysts was found to be dependent on several factors, however, the release was dominated by the microbial growth. The microbial Mo release is a rapid process, requiring less than one week for 90% of the releasable Mo to be solubilized from the THF washed uncrushed catalyst. It is expected that the recovery would be even greater with crushed catalyst. The THF was judged to be the best solvent for the metal recovery. Also. leaching rates were significantly greater for the crushed catalyst.

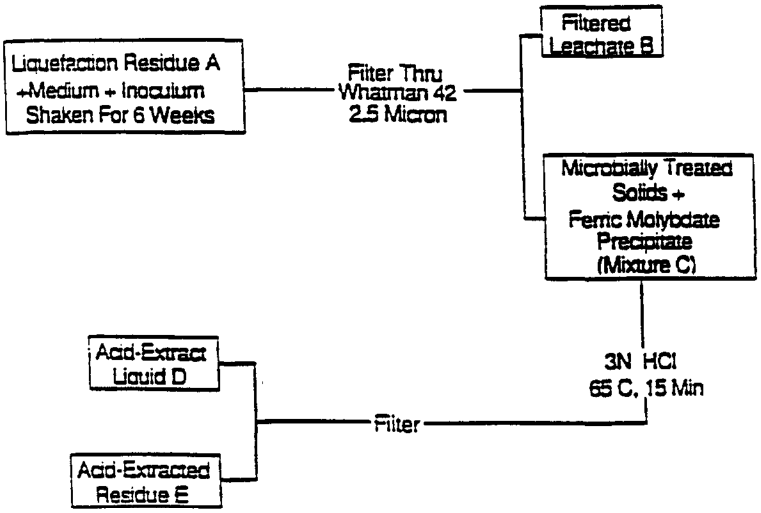

Fig. 31. Simplified flowsheet of shake-flask bioleaching experiments [143].

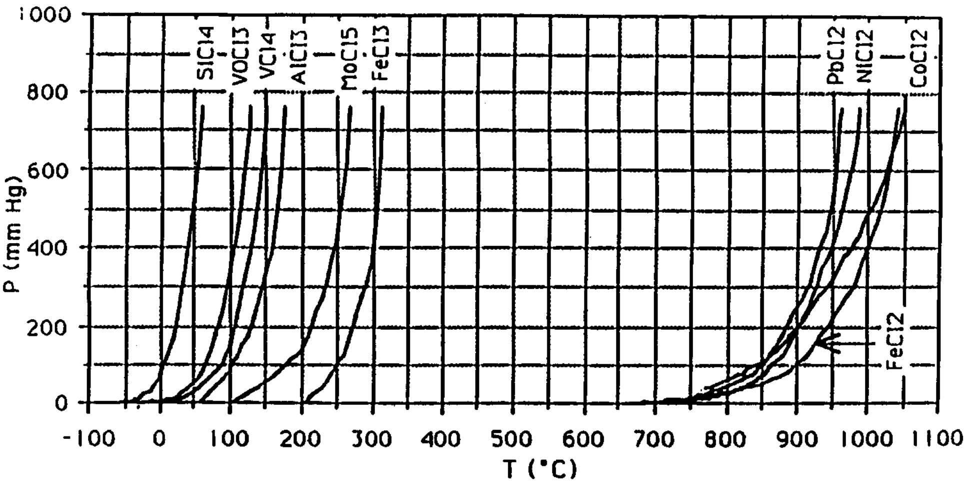

Fig. 32. Vapour pressure of some metal chlorides and oxychlorides [148].

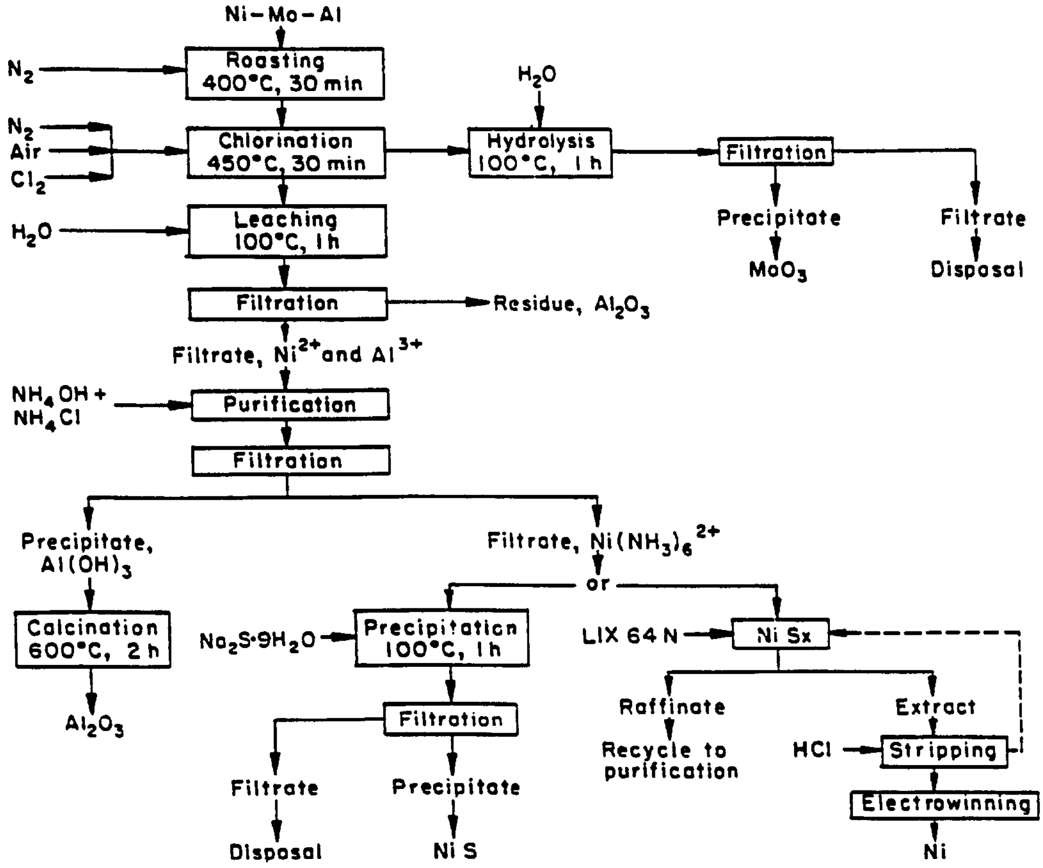

Fig. 33. Flowsheet of anhydrous chlorination process for spent NiMoAl catalyst [149].

4.1.1.3. Chlorination. This process is based on the difference in volatility of the metal chlorides and/or oxychlorides. Thus, the results in Fig. 32 show that a good separation of Mo and V from Co and Ni can be achieved if a proper chlorination temperature is chosen [148,149]. The major chemical reactions which occur during chlorination of spent Ni(Co)-Mo/Al_2O_3 and Ni-W/Al_2O_3 catalysts were formulated by Jong et al. [124] as follows:

$$MoO_3 + C + Cl_2 + 1/2O_2 \rightarrow MoO_2Cl_2 \uparrow + CO_2$$

$$WO_3 + C + Cl_2 + 1/2O_2 \rightarrow WO_2Cl_2 \uparrow + CO_2$$

$$2NiO + C + 2Cl_2 \rightarrow 2NiCl_2 + CO_2$$

$$2CoO + C + 2Cl_2 \rightarrow 2CoCl_2 + CO_2$$

$$2Al_2O_3 + 3C + 6Cl_2 \rightarrow 4AlCl_3 + CO_2$$

The chlorination was carried out in a fluidized bed between 400 to 600°C using various mixtures of Cl_2 containing N_2, CO air and CO_2. Volatile MoO_2Cl_2 and/or WO_2Cl_2 were condensed in the primary and secondary receivers. Prior to chlorination, the spent catalysts were roasted at 400°C to remove moisture and other volatiles. After chlorination, the Mo- and W-containing chlorides were washed out from the receivers and the lines. The slurry containing volatile chlorides was filtered and the filter cake hydrolyzed at 100°C and 20°C to isolate Mo- and W-containing chlorides, respectively. To recover Ni and Co, the spent charge from the chlorination process was water leached at 100°C for 1 h. Filtered leach solution was used for recovery of Ni and Co. The detailed flowsheet of the process is shown in Fig. 33. As the results in Table 20 show, the chlorination may be suitable method for metal recovery. Final recovery of metals was 65 to 99%.

Table 20
Typical metal recovery by chlorination [148]

Spent catalyst		Recovery (wt%)					
		Ni	Co	Mo	W	V	Al
Ni-Mo-Al_2O_3							
	A	83		89			4
	B	84		95			11
Ni-W-Al_2O_3							
	C	73			82		5
	D	79			98		27
Co-Mo-Al_2O_3							
	E	99	99	94		98	36

The chlorination procedure patented recently can be used for recovery of transition metals from the refractory and spent catalysts [150]. This process employs various chlorination mixtures, i.e. chlorine + air, chlorine + inert gas, chlorine + inert gas + reducing gas or chlorine + inert gas + air. Temperatures vary between 250 and 600°C and a total pressure of 10 to 300 kPa. Gaballah and Djona [148,149] achieved an

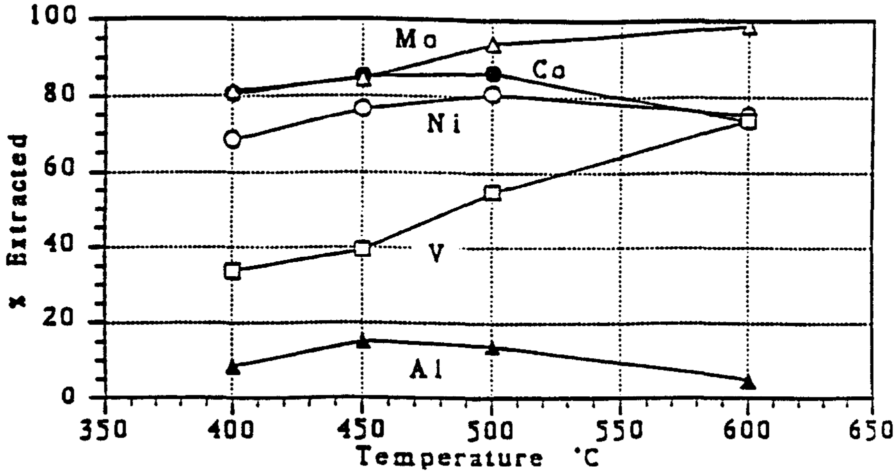

Fig. 34. Effect of temperature on extraction of metals during carbochlorination of roasted catalysts in 50% N_2 + Cl_2/CO = 3 [150].

optimum of chlorination at 600°C using a gas mixture containing 50 to 67% N_2 and a Cl_2/CO ratio of about 3. Effect of temperature on metal recovery using the gas mixture containing 50% N_2 is shown in Fig. 34. Under these conditions about 99% Mo and 74% V could be extracted from the condensate. About 75% Co and 85% Ni were extracted by leaching the chlorination residue. Chlorination in Cl_2–air mixture was ineffective, whereas using the N_2–Cl_2 mixture, about 95% Mo and 65% V could be recovered. These authors further observed that roasting temperature had an effect on the yields. The best recovery was achieved when the catalyst was roasted (prior to chlorination) at 500°C.

Table 21
Efficiency of metal recovery from roasted and unroasted catalysts [151]

Catalyst	Process	Temp. (°C)	Recovery (wt%)				
			Co	Ni	Mo	V	Al
Unroasted	Chlorination: Cl_2-O_2-N_2, N_2 = 0–67%	380–500	91.8	96.5	95.3	70.9	9.6
Roasted	Chlorination; Cl_2-CO-N_2 N_2 = 33–67	400–600	80.9	76.3	90.5	51.4	9.7
Unroasted	Two-step leaching: NaOH-H_2SO_4	80	64	57	83	61	15

Gaballah and Djona [151] expanded their chlorination studies to include recovery of metals from a spent-unroasted hydroprocessing catalyst. As the results in Table 21 show, the efficiency of metal recovery from the unroasted catalyst was higher than that from the roasted catalyst under properly chosen chlorination conditions. Also, the chlorination process was much more efficient than the two-step leaching process.

4.1.1.4. Electrochemical dissolution. A new process developed at Batelle uses catalyzed

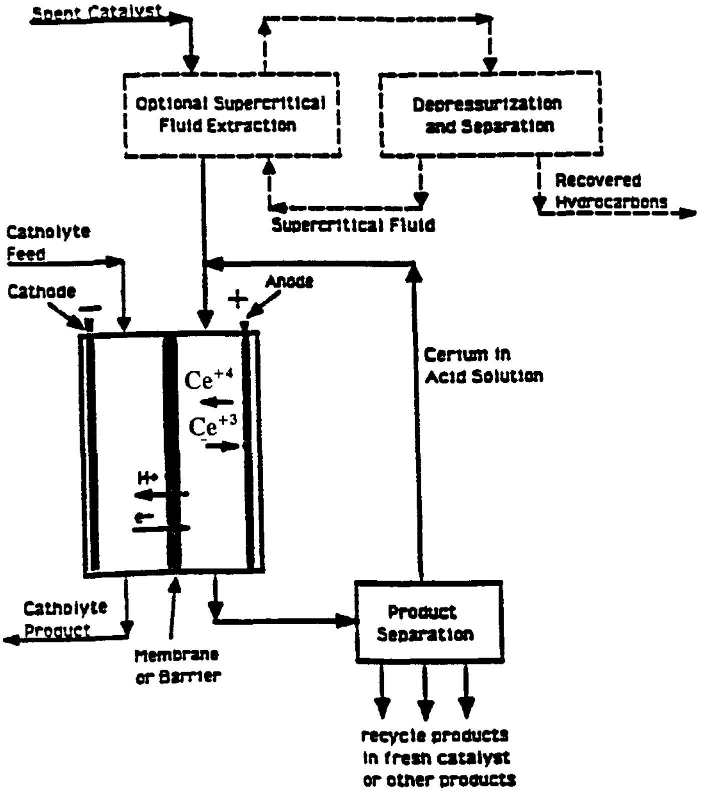

Fig. 35. Schematic of catalyzed electrochemical dissolution [152].

electrochemical dissolution to remove (oxidize) most of the coke and dissolve metals in an aqueous solution for further recovery [152]. The schematics of this process, which operates at moderate temperatures and ambient pressure, are shown in Fig. 35. In this process, the spent catalyst is added to the solution containing a strongly oxidizing ion such as Ce^{4+}. The solution is added to the anode side of the electrochemical cell. Here, aqueous Ce^{3+} is oxidized to Ce^{4+} which in turn oxidizes coke to CO_2 and H_2O and metals to soluble metal species. A typical anodic oxidation of MoS_2, which is the main component of spent hydroprocessing catalysts proceeds in the following way:

$$MoS_2 + 12H_2O \rightarrow MoO_4^{2-} + 18e^- + 2SO_4^{2-} + 24H^+;\ E^0 = -0.43V$$

Other metal sulphides which are part of spent catalysts can be oxidized in a similar manner. Although most of the coke can be removed by the anodic oxidation, the efficiency of the process is improved by coke removal using supercritical extraction prior to the electrochemical dissolution. For this purpose, the authors used CO_2 alone and in the mixture with toluene, as well as propane alone and in the mixture with THF and acetone.

Silva et al. [152] conducted an experiment using a solution of Ce^{4+} in nitric acid. In this case, most of the solids dissolved in about 20 min. Another experiment was conducted in which spent catalyst was contacted with the solution of nitric acid without Ce^{4+} over night. The catalyst did not dissolve under these conditions but it dissolved within a few minutes after the addition of Ce^{4+} to the solution. When nitric acid was replaced by sulphuric acid, the catalyst dissolved only partially and other solid phase, presumably ceric sulphate precipitated. A patent application filed by Battelle was based on this study [153].

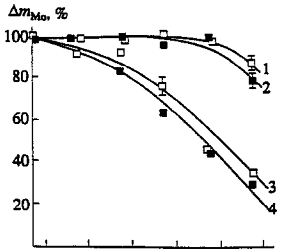

Fig. 36. Molybdenum-mass change versus NiMoAl treatment temperature and time [154]: 1, 10 min thermal treatment; 2, 15 min thermal treatment; 3, 10 min radiation thermal treatment; 4, 15 min radiation thermal treatment.

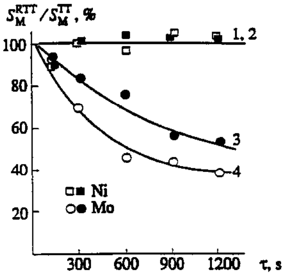

Fig. 37. Effect of duration of 1.2 MeV fast electron treatment on the amount of Ni- and Mo-containing phases in the irradiated NiMoAl catalysts at 1073 K (1,3) and 1173 K (2,4) [154].

4.1.1.5. Radiation-thermal treatment. Lunin et al. [154] reported on the behaviour of spent Ni(Co)-Mo/Al_2O_3 catalysts under conditions of the thermal and radiation-thermal treatments in the air. For the latter, 1.2 MeV electron beam accelerator was used. The radiation treatment resulted in crystallization of new phases at much lower temperatures than it is usually observed during the oxidative catalyst regeneration. MoO_3 was the predominant phase in the irradiated catalysts. As the results in Fig. 36 show, the sublimation of MoO_3 was significantly enhanced by the radiation treatment. Thus, the sublimation temperature was decreased by almost 300°K. The yields of MoO_3 exceeded the amount of MoS_2 in the spent catalyst suggesting that some other Mo containing phases in the catalyst were also converted to MoO_3. The results in Fig. 37 show that the behaviour of Ni differed markedly from that of Mo. The same observation was made also for the Co-Mo/Al_2O_3 catalyst. Based on this difference, a high purity MoO_3 can be recovered for recycling. It appears that a commercial viability of this approach has not yet been assessed.

The methods employing thermal plasma may also be included in the category of methods based on the radiation-thermal treatment. A high energy density, high temperatures and flexibility in the plasma gases employed are among advantages of this method. Potential of this method for recovery of metals from spent catalysts was indicated by Burkhard et al. [155].

4.1.2. *Other potential applications*

A possibility of using, at least a small portion of spent catalysts for preparation of construction materials would be the area to explore. Also, depending on the remaining porosity and surface area, spent catalysts may still have potential especially, in some gas–solid applications.

4.1.2.1. Construction materials. Spent catalysts from industrial processes are among 9 types of waste solids listed by Schreiber and Yonley [156] as having a potential to be utilized for cement production. While this may be true for the spent FCC catalysts, no indication is given on a similar application of spent hydroprocessing catalysts. It is believed that for the latter this application has only a remote chance. Some information suggests that spent FCC catalysts can be used for preparation of red bricks and as asphalt filler [12]. Although, in this case, there is no information to indicate that this application may have a better chance in case of spent hydroprocessing catalysts. Nevertheless, the most recent information indicates on the EPA proposal [157] to prohibit the use of hazardous wastes as the fill materials. If implemented, this action would diminish and/or completely eliminate construction materials as an option for utilization of spent hydroprocessing catalysts.

4.1.2.2. Catalyst preparation. The cascading of spent catalysts, i.e. their reuse in the low severity operations is a well established approach. In one example, a spent catalyst used in an HDS operation was used for hydrocracking of vacuum residues in a suspended bed reactor [158]. The catalyst exhibited rather good performance in spite of a heavy contamination, i.e. 9.6 wt% V, 6.0 wt% Ni and 12.9 wt% carbon. Sakabe and Yagi [159] used a tubular type reactor to evaluate a spent HDS catalyst for hydroprocessing atmospheric and vacuum residues. Activity of the spent catalyst for hydrocracking was rather high. In a similar study published by Mittal et al. [160], a spent-regenerated catalyst, after more than four years of the useful lifetime in an HDS operation, was used for mild hydrocracking of a vacuum residue. The marginal cost of the catalyst, low H_2 pressure employed and high yields of middle distillates suggest that this option may be economically attractive. Interestingly enough, spent catalyst from the residue upgrading was used for HDS of a naphtha fraction [161]. The purpose was to selectively remove sulphur while avoiding the olefin hydrogenation to minimize the loss of octane level. In this regard, the spent catalyst exhibited a good performance. It is believed that the cascading can be further expanded to include non-refinery applications. Thus, in spite of the loss of activity for hydroprocessing, the spent-decoked catalysts may still possess adequate porosity and surface area, e.g. for various gas–solid applications. The presence of Ni and V offers a possibility of utilizing the spent catalysts in hydrogenation and oxidation reactions, respectively. Various types of Mo- and W-containing catalysts are also known.

Of course, if metals can be isolated from spent catalysts in a relatively pure form, they can be used again for the preparation of hydroprocessing catalysts [162]. Other types of catalysts may also be prepared. For example, Lee et al. [163] reported on the preparation of reforming catalysts using the V and Ni loaded extract obtained from spent catalysts. The extraction was performed using 10% citric and 8% oxalic acids at about 100°C. The content of some metals in the extracts are shown in Table 22. Thus, while the content of V was similar in both extracts, that of Mo and Ni was significantly greater in the citric acid extract. Both extracts were used to impregnate a high surface

Table 22
Metal content in acid extracts (ppm) [163]

	Citric acid	Oxalic acid
Al	6200	7150
Ca	292	164
Co	692	0
Fe	2650	20
Mo	1530	167
Na	639	489
Ni	15000	111
P	123	59
Si	715	616
V	21000	18000
Zn	183	0

amorphous silica support. After additional thermal treatments, the catalysts were tested for their dehydrocyclization activity using *n*-octane as a model compound. The catalyst prepared from the low Ni and Fe extract exhibited high activity whereas the presence of Ni and Fe favoured dehydrogenation and cracking.

Other information indicates that the traditional Co-Mo/Al_2O_3 catalyst, after being regenerated, was used for reducing sulphur oxides to elemental sulphur [164]. However, no details on the type of chemical process are given in this brief information. The spent Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 catalysts, after being regenerated, were used to catalyse the decomposition of H_2S [165]. As the results in Fig. 38 show, the decomposition of H_2S in the mixture of 10 vol% H_2S and CH_4 balance, was significantly enhanced in the presence of the catalyst. Thus, in the absence of the catalyst, the H_2S decomposition was negligible. Presulphiding the regenerated catalysts had little effect on the decomposition. Also, the Co-Mo/Al_2O_3 catalyst was more active than the Ni-Mo/Al_2O_3 catalyst. One may suggest that above 600°C, a sintering of catalyst may take place. However, considering the low cost and a good performance, the catalysts show promise for similar applications. Perhaps, a number of other catalytic applications for the spent and properly treated catalysts may be found.

4.1.2.3. Hot gas clean-up sorbents. The analysis of spent-regenerated catalysts shown in Table 11 indicates the presence of several metals which have rather high affinity for H_2S. This is given by the high driving forces for the reaction of metal oxides with H_2S, shown in Table 23. Commercial hot gas clean-up sorbents usually contain oxides of Fe, Zn, Ca, Ni and Cu [166]. It is evident that oxides of Mo and W can also be suitable materials. Moreover, the spent-re-

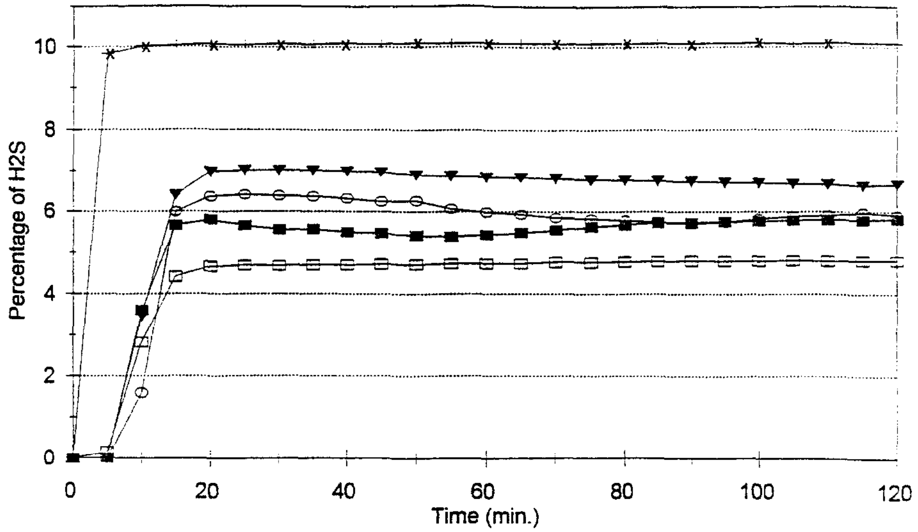

Fig. 38. Effect of temperature on decomposition of H_2S: ×, 550°C no catalyst; ▼, 550°C; ■, 600°C; ○, 650°C; □, 600°C fresh catalyst.

Table 23
Free energies ($-\Delta G$) for reaction of metal oxides with H_2S

Temperature (K)	800	900
$MoO_3 + CO = MoO_2 + CO_2$	27.3	29.9
$MoO_2 + 2H_2S = MoS_2 + 2H_2O$	21.4	16.7
$CoO + H_2S = 1/9Co_9S_8 + H_2O + 1/18S_2$	14.3	14.2
$NiO + H_2S = 1/3Ni_3S_2 + H_2O + 1/6S_2$	11.4	12.0
$ZnO + H_2S = ZnS + H_2O$	17.7	17.7
$Fe_3O_4 + 4H_2S = FeS + FeS_2 + FeO + 4H_2O$	21.6	22.9
$FeO + H_2S = FeS + H_2O$	10.2	10.3

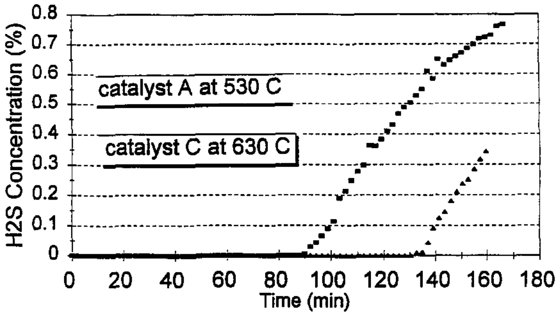

Fig. 39. Cleaning efficiency of spent-decoked catalysts (catalyst A, CoMoAl; catalyst C, NiMoAl) [168].

generated catalysts possess relatively high surface area compared with commercial sorbents. Thus, for the former, the surface area may be higher than 100 m^2/g compared with less than 10 m^2/g for zinc-ferrite, which is the best known commercial hot gas clean-up sorbent. In case of the molten carbonate fuel cell technology, the hot gas clean-up is conducted at about 550°C [167]. It is believed that at about such a temperature, the spent-regenerated catalysts can be used as hot gas clean-up sorbents in several successive utilization–regeneration cycles before their surface area declines to the level of some commercial sorbents, e.g. zinc ferrite. The analyses of several spent-decoked hydroprocessing catalysts (Table 11) show that some precautions must be taken while selecting the spent catalysts for hot gas clean-up sorbents. Thus, in some cases the presence of species such as P and As may require some attention. It is believed that Pb will not interfere because of its high affinity for sulphur yielding PbS. which has rather low volatility. However, most of the spent hydroprocessing catalysts do not contain P and the content of As may also be very low. Nevertheless, this issue should not be underestimated.

Three spent catalysts were decoked under controlled conditions to remove coke prior to their use as hot gas clean-up sorbents. The metal analysis of these catalysts is shown in Table 24. The Co-Mo/Al_2O_3 catalyst was microporous HDS having an extrudate form, whereas one of the Ni-Mo/Al_2O_3 catalysts was a macroporous chestnut bur like HDM catalyst, and the other, a trilobe form of an HDS catalyst [168]. The efficiency of these catalysts for removal of H_2S from a simulated coal gasification mixture was compared with that of zinc-ferrite. It is believed that several gaseous byproducts generated in refinery operations may also require sulphur removal prior to their utilization. The results for two spent-decoked catalysts are shown in Fig. 39. Such results were

Table 24
Composition of spent (S) and spent-decoked (SD) catalysts [168]

	Catalyst A		Catalyst B		Catalyst C	
	S	SD	S	SD	S	SD
Carbon	7.7	nd	26.2	nd	7.4	nd
Hydrogen	0.8	nd	3.5	nd	1.2	nd
Nitrogen	0.14	nd	0.27	nd	0.4	nd
Sulphur	6.23	nd	5.5	nd	7.1	nd
Mo	9.30	9.97	5.36	7.67	8.87	9.70
Ni	< 0.01	< 0.01	2.12	3.34	2.65	2.86
Co	2.9	3.1	nd	nd	nd	nd
Fe	< 0.05	< 0.05	0.04	0.06	0.08	0.1
V	< 0.01	< 0.01	2.67	4.02	0	0

Table 25
Breakthrough times for fresh (F) and spent-decoked (SD) catalysts and sorbent (min) [168]

Temperature (°C)	Weight used (g)	Breakthrough time *A*	*A*[a]
Catalyst A/F			
530	5.0	132	152
630	5.0	170	196
Catalyst A/SD			
530	5.0	90	101
630	5.0	105	118
Catalyst B/F			
530	2.0	44	165
630	2.0	48	180
Catalyst B/SD			
530	2.0	33	77
63	2.0	24	56
Catalyst C/SD			
530			
630	2.0	47	149
Zinc ferrite			
530	1.0	170	170
630	1.0	180	180

[a] Results normalized to the same amount of active metals as in 1 g of zinc ferrite.

used for estimating breakthrough times by extrapolating the steepest part of the curves in Fig. 39 to zero H_2S concentration. These results are summarized in Table 25. The last column indicates the breakthrough times when normalized to the amount of active metals contained in a unit of zinc ferrite. It is evident that some spent-decoked catalysts (e.g. catalyst C) can be an efficient sorbent, especially if the cost of commercial sorbents is taken into consideration. Thus, spent hydroprocessing catalysts are classified as hazardous solids and as such they are available either at no cost or even with some financial incentives if taken from the refinery.

4.2. Spent FCC catalysts

Typical equilibrium (spent) FCC catalysts and catalyst fines contain about 60 wt% SiO_2 and about 40 wt% Al_2O_3 in addition to a relatively small amount of contaminants. Regeneration is always an integral part of all FCC units [5]. However, regeneration can remove only the deposited coke. The catalyst activity decline, which is mostly caused by the deposited metals, is usually offset by periodically withdrawing a portion of the spent catalyst and replacing it with the fresh catalyst.

Attempts are being made to develop a procedure for separation of the active and inactive catalyst particles, which are part of the equilibrium FCC catalyst prior to shipment for disposal or utilization. In this regard, the magnetic separation technique has been evaluated [40]. The schematic of the open gradient version of this technique is shown in Fig. 40 [169]. In this process, dry catalyst particles are dropped through an open bore. A super conducting quadrupole magnet creates a very steep gradient across the bore. This forces paramagnetic materials containing metal contaminants to move to the outer circumference whereas diamagnetic particles move towards the center of the bore. This system can operate in a continuous mode using multiple stages of separation. The patent disclosed by Doctor [170] is also based on a magnetic beneficiation of FCC catalyst containing more than 1000 ppm Ni. In this case, the spent catalyst is separated into several zones. The first zone contains more than 6000 ppm of Ni, two other zones have Ni equivalents in the

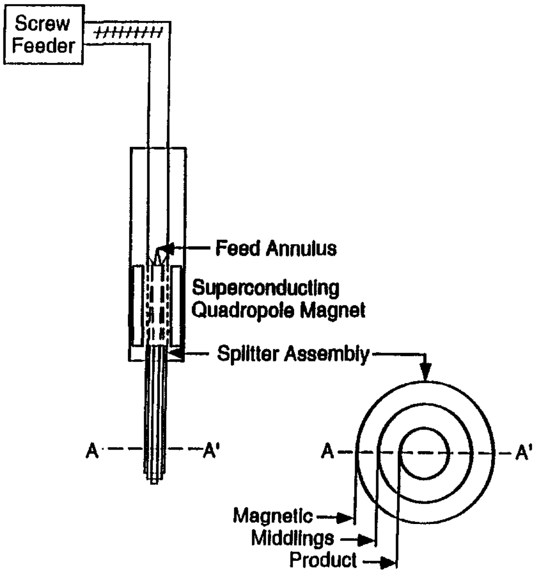

Fig. 40. Schematic of open gradient magnetic separation method [169].

range of 2000 to 6000 ppm and about 2000 ppm and less, respectively. After these zones are separated, the uncontaminated portion of the catalyst is returned to the operation.

Another demetallation process is based on the addition of a metal getter additive, with higher settling velocity to the regenerator [171]. The metals are then removed by solid–solid interaction. The uncontaminated portion of the FCC catalyst, forming a light discrete zone on top of a more dense zone of the additive, is then recycled to the operation. The additive with adsorbed metals is withdrawn from the lower part of the fluidized bed. A process disclosed by Chevron [172] can demetallize spent FCC catalyst containing up to 10 000 ppm of the contaminant metals in an external reactor by contacting the spent catalyst with the additives containing Ca or Mg, i.e. dolomite and sepiolite, respectively. The addition of Sb and Bi to the metal getters may improve the efficiency of demetallation. The contact is made at about 730°C in the presence of steam. It is believed that metal concentrates obtained by these methods, as well as that obtained by magnetic separation technique, are suitable for metal reclamation.

A detailed evaluation of the spent FCC catalysts and solid by-product should always be conducted to ensure the technical and environmental acceptability and to establish optimal

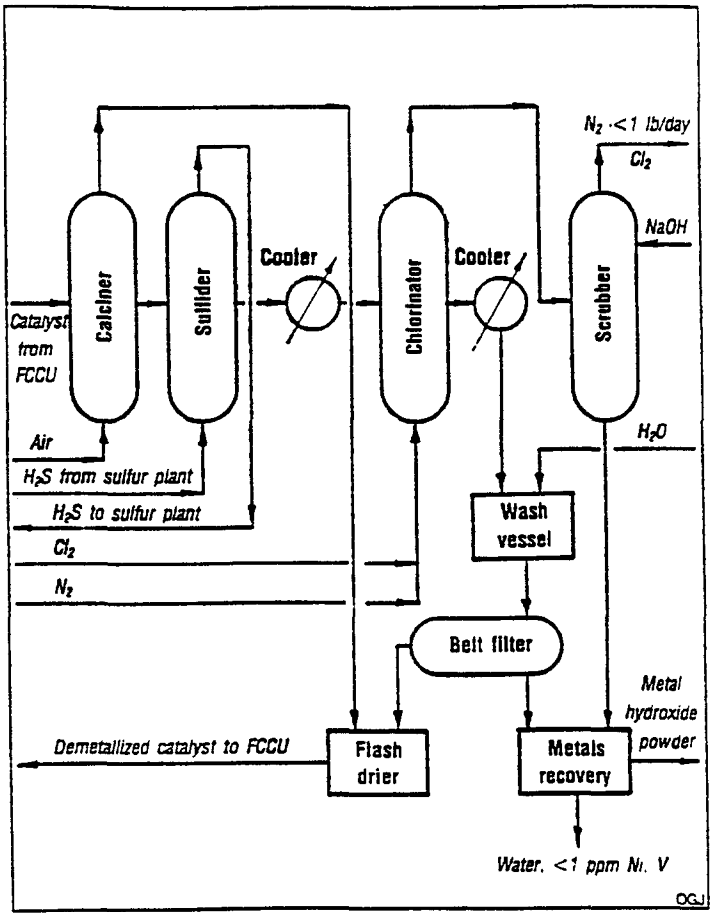

Fig. 41. Flow diagram of DEMET demetallization process [174].

schemes for utilization and disposal. A predominant use of spent FCC catalyst is in the area of construction materials such as the filler for asphalt as well as the production of brick and cement. In this case, physical and structural properties of the product must not be affected by addition of the spent catalysts. From the environmental point of view, the products should be non-leachable and should not release any poisonous gases during the life cycle.

The proximity of the spent catalyst source to the point of use may be important because this determines the transportation cost. For example, because of a suitable location, one refinery in the USA sells more than 5000 metric tons of the spent FCC catalyst and fines annually to industrial customers [63]. According to Schmitt [12], the usages of spent FCC catalysts in the area of construction materials in Europe exceed the supply by the refineries. The disposal is the last alternative if no industrial outlet can be found.

4.2.1. *Metal reclamation*

The content of contaminant metals in spent FCC catalysts is significantly lower than that in hydroprocessing catalysts. Nevertheless, there is an incentive to remove metals such as V and Ni and return the FCC catalyst to the operation for reuse. The removed metals can be sold to metal reclaimers. This can be achieved by the DEMET process which is now being used commercially. The detailed description of this demetallization process, the flow diagram of which is shown in Fig. 41, was given by Elvin and Pavel [173]. The process consists of two main sections, i.e. the reactor section followed by filtration and drying sections. The process begins with introducing the spent FCC catalyst to the DEMET calciner for coke removal. The decoked catalyst flows by gravity to the sulphiding reactor, where it is sulphided with H_2S. The cooled sulphided catalyst flows to the chlorinator where metal sulphides are converted to chlorides by treating with the chlorine. The V and Fe chlorides are vaporized from the catalyst and subsequently scrubbed from the gas in the scrubber. After cooling, the chlorinated catalyst is slurried with the water and transported to the filtration section where the slurry is filtered using a belt filter. The filtered catalyst cake is sent to the flash drier. The dried demetallized catalyst is returned to the FCC operation. The filtrate from filtration and the chlorinator overhead scrubber solution are sent to the metal recovery unit where by adjusting pH, pure metal hydroxides can be recovered. The dried metal hydroxides are sold to metal reclaimers. The commercial results published by Elvin and Pavel [174] indicate a significant impact of the DEMET process on the operation of FCC units. For example, the catalyst consumption was reduced by about 50%. Among ambitious objectives set by these authors is the elimination of the catalyst disposal by further increasing the volume of the demetallized FCC catalysts. It is believed that there is a potential to combine the magnetic separation of non-active catalyst particles from the active particles shown in Fig. 40 with the DEMET process. Therefore, almost total elimination of the catalyst disposal appears to be achievable.

Another method for metal recovery is based on treating spent catalysts with a flux such as a Group IA or IIA metal and a phosphate containing compound [175]. The metals are then recovered as metals or metal phosphides in a distinct layer. The accumulated metals can then be further processed and recovered.

4.2.2. *Construction materials*

4.2.2.1. Asphalt filler. The ASTM specifications include a number of asphalt products requiring fine fillers. A typical asphalt product contains about 90% gravel, 5% bitumen and 5% filler. In case of the filler, particle size plays a key role. Some spent FCC catalysts and fines can meet these specifications. In another case some milling may be required to obtained prescribed particle size distribution. It appears that the amount of filler to be used depends on the content of contaminants and/or passivator. Thus, up to 5% of the spent FCC catalyst can be used as filler when Sb content is lower than 600 ppm [12]. Otherwise, the proportion of the spent catalyst should not exceed 3 wt%.

4.2.2.2. Cement production. The cement production may be perhaps the most attractive outlet for spent FCC catalysts. Thus, a typical plant manufactures about 2000 tons of cement per day utilizing about 3000 tons per day of raw materials [156]. The cost of transportation may be important for choosing this utilization option. Thus, an ideal case would be a refinery employing the FCC technology and a cement manufacturing plants in the same location. In any case, the spent FCC catalysts may represent only a very small fraction of total material requirements of the cement plant. In some cases, the spent FCC catalysts may require some pretreatment before being used for cement production.

The spent catalysts and fines are valuable to the cement industry as a raw material because of their content of silica and alumina. In a cement kiln at high temperatures, silica and alumina react with lime to produce Portland cement. The spent catalyst can account for up to 6% of the cement raw material. The rest is lime and clay accounting for about 75 and 19%, respectively. A leaching test on clinkers containing spent FCC catalysts confirmed that these solids are non-hazardous [12].

Prior to their use in cement production, the spent FCC catalysts must be subjected to a detailed analytical evaluation [156]. The analytical results are documented on a waste profile form. The attention is paid to cement constituents and impurities. Only after a detailed evaluation, the cement chemist responsible for the manufacturing recipe can determine how much of the spent FCC catalyst can be added to the process. If spent catalysts fail prescribed parameters, they can not be approved for use in the cement production. For example, presence of the alkalis may have detrimental effects because they promote undesirable agglomeration of the cement during the curing stage. Some cement plants will not take spent FCC catalysts because they are already at the alkali limit with the base feedstock.

4.2.2.3. Brick production. As reported by Schmitt [12], extensive production trials were conducted in Europe on utilization of the spent FCC catalysts for the production of bricks. The quality of bricks was found to be satisfactory when 5% of the spent catalyst was added. Also, a detailed analytical evaluation confirmed that bricks are fully environmentally acceptable. Moreover, the tests confirmed the retention of all metals of concern under the processing conditions, i.e. during the brick firing. In spite of the positive results, this utilization option of spent FCC catalysts has not yet found industrial applications because the brick manufacturers could not be guaranteed a steady long term supply of large volumes of spent FCC catalysts.

4.2.2.4. Ceramic frits. Frits are materials of a vitreous nature used for glazing ceramic tiles. Escardino et al. [176] compared the quality of the frits prepared from the spent FCC catalysts with those prepared from kaolin and other materials used for the frit preparation. No important differences were observed between the aesthetic and technical characteristics of the glazes (e.g. whiteness, gloss, microhardness, etc.) prepared from the spent FCC catalysts compared with the glazes prepared from standard materials.

4.2.3. Catalyst development

A temporary utilization of spent FCC catalysts in less severe refinery operations may be the first option to be explored. Moreover, as was shown in the study published by Itoh and Sue [177], even preparation of some new catalysts from spent FCC catalysts is not impossible. These authors used a spent FCC catalyst to develop an active catalyst for a new mild residue hydrocracking process. In this case, a spent decoked FCC catalyst was mixed with a spent crushed HDS catalyst. A slurry of this mixture with a vacuum residue was then heated and pumped in the hydrocracking reactor. Perfor-

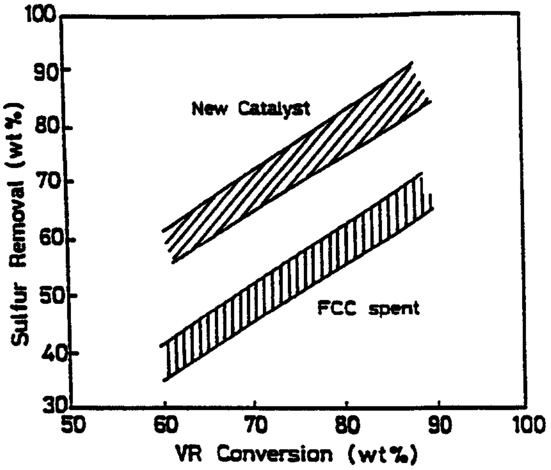

Fig. 42. Sulphur removal during hydroprocessing of vacuum residue using new and spent FCC catalysts [177].

mance of the new catalyst, i.e. 80% FCC and 20% HDS mixture is compared with the spent FCC catalyst in Figs. 42 and 43. It is believed that the spent FCC catalyst portion of the new catalyst was acting as a coke getter and provided a cracking activity, whereas a portion of the spent HDS catalyst provided necessary hydrogenation activity. The reactor effluent contains the gaseous and liquid products and the catalyst with the coke. The solids can be separated either by centrifuging the wet cake in a rotary dryer, or by distillation. Dry catalyst and coke flow to the fluidized bed regenerator and subsequently returned to the hydrocracking process.

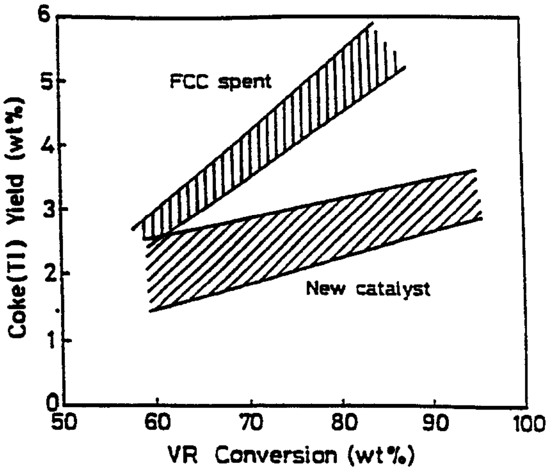

Fig. 43. Coke formation on new and spent FCC catalysts during hydroprocessing of vacuum residue [177].

The process for hydrocracking residues and heavy oils based on the reuse of spent-regenerated FCC catalyst claimed by McHenry [178] may be used as an example of cascading. Also, Mobil Oil Corp. [179] has recently patented a process in which the spent FCC catalyst is used for processing refinery sludge and slop oils. In this process, the hot spent FCC catalyst can demetallize and deemulsify the waste streams in an auxiliary reactor without contaminating or interfering with the FCC catalyst inventory. After being processed, the refinery sludge and slop oils can be further processed in the FCC reactor. In some cases, the auxiliary reactor and FCC reactor may share a product fractionator. A recently disclosed process employs the spent FCC catalyst for low cracking or recracking of naphtha fractions to lighter products [180]. Also, the method improves the octane number of the cracked naphtha.

4.3. Recovery of precious metals from reforming catalysts

The primary purpose of reforming is the increased octane number of gasoline to improve engine performance. This is achieved by converting paraffines to iso-paraffines as well as naphthenes to aromatics. The naphtha fraction is usually the primary feedstock. The current trends in gasoline specifications, involving a gradual decrease in the content of aromatics, indicate a decreasing importance of reforming and its potential replacement by other technologies, e.g. alkylation, isomerization and polymerization. Nevertheless, the reforming units still represent an important part of many refineries around the world. In fact, the recent information [181] suggests that new reforming units are still being constructed in some parts of the world. Thus, the management of spent reforming catalysts will continue to require a special attention compared with the other spent solid refinery catalysts.

Some of the platinum group metals (Pt, Re, Ir, Os, Pd, Rh and Ru) are an essential part of the reforming catalysts. Similarly, as in automobile and isomerization catalysts, these metals are always combined with support such as alumina or carbon to improve their utilization during the operation. Replacement after catalyst deactivation depends on the type of catalyst and operating conditions. It was indicated that more than 100, and in one case, almost 226 regeneration cycles could be performed before catalyst replacement was necessary after more than 5 years [182]. Problems encountered during the regeneration of spent reforming catalysts were discussed extensively by Fung [183] and Beltramini [184]. Once the regeneration becomes uneconomical the spent catalysts are shipped to a metal reclaiming company. It is quite obvious that recovery of the metals from the spent reforming catalysts is the only option. It is unlikely that there is an option which can compete with the recovery, although a cascading may have potential in some specific situations. Jacobsen [185] maintains that despite the extreme price, the use of Pt group metals can be cost effective because they can be economically recovered for reuse.

The high value of Pt group metals dictates that refineries must pay some special attention to the proper handling and inventory of the spent reforming catalysts. It is essential that detailed records of all events (before, during and after the operation), involving reforming catalysts, are maintained. In this regard, an accurate chemical analysis determining the content of the metals should be the very first step after the shipment is received, after the removal from the operation and/or before being shipped to the regenerator or metal reclaimer. This also requires a reliable and precise analytical technique. Thus, it was shown by Rosso [10,186] that in the case of Pt, a tolerance of ±0.5% may represent a significant monetary value. The development of an accurate and rapid analytical method for determining precious metals is still attracting the attention of some researchers. Further, careful sampling, assaying and accounting is essential for the effective recovery of precious metals. In this regard, it is important to distinguish between the different fractions of spent catalyst particles, i.e. oversize, primary catalyst and fines. Usually, a sample of spent catalyst is analyzed by the refiner and the reclaiming company. A common settlement/decision is then sought between the parties. All precautions, which have to be taken during all stages of handling and utilization of reforming catalysts were described in details by Rosso and El Guindy [186]. Thus, as pointed out by Jacobsen [185], ten tonnes of the wet Pt bearing spent catalyst may contain some 100 kg of Pt. In monetary terms, this represents more than $ 1 000 000. Therefore, all efforts to monitor the inventory of the spent reforming catalyst are worthwhile.

A partial removal of the contaminants which were deposited on the catalyst during the operation is an important step before metal recovery is carried out. A catalyst can not be accurately sampled and properly handled if it is covered with a large amount of the residual carryovers. Also, costs of metal reclaiming from such catalysts are much higher. It may be advantageous for the refiner to have the spent reforming catalyst decoked before being shipped to the reclaiming company. In this regard, the procedure applied during catalyst withdrawal from the reactor may be important. Then, removal of the residual coke may be achieved quite readily by applying the same procedure as used for the regeneration, i.e. by the controlled burnoff [183,184]. An accurate inventory and proper sampling of the spent reforming catalysts can be achieved only after decoking. Also, most of the methods used for recovery of the Pt group metals from the spent catalysts require decoking as the first step.

The continuous catalyst regeneration is part of some reforming systems. In this case, spent catalyst is withdrawn from the reactor and transported to the regenerator, where the carbon is burned off and the catalyst reconditioned. A small fraction of the catalyst, known as heel catalyst, is held at the bottom and along the walls of the reactor. Over time, the carbon level of this non-flowing catalyst may approach 50 wt%. The heel-contaminated catalyst cannot be properly regenerated and reused. Therefore, metal recovery appears to be the only solution. It was shown by Blashka et al. [187] that a light fraction of the catalyst can still be recovered from the heel catalyst by the gravity separation. The recovered light fraction is then reused, whereas the heavily contaminated fraction is sent for metal recovery.

Reclamation procedures used for the recovery of precious metals from catalysts used in automobile converters were reviewed by Mishra [188]. Recovery of precious metals from non-catalyst sources was extensively reviewed by Harris [189]. In the latter review, very useful information on solvent extraction, as applied to Pt group metals, is also presented. It is believed that the processes applied for the recovery of Pt group metals from spent automobile catalysts can be applied for that from the spent reforming catalysts in spite of some differences in the structure. Thus, besides a different shape, the former were exposed to much more severe conditions than reforming catalysts. For example, temperatures exceeding 1100°C during the use of the automobile catalysts are not unusual. This will inevitably cause a total transformation of gamma-alumina, which is the original form of alumina in the catalyst, to other forms of alumina. The recovery of metals from extensively sintered solids will be more difficult than that from spent reforming catalysts. One may assume that recovery of the precious metals from severely deactivated/damaged reforming catalysts, may require similar conditions as that from the spent automobile catalysts.

4.3.1. Hydrometallurgical processes

It appears that hydrometallurgical processes are the most widely used for recovery of metals from the spent reforming catalysts. Both the support and metal dissolution methods are applied. Some innovative processes are emerging as well.

4.3.1.1. Dissolution of support. Rosso and El Guindy [186] described recovery of Pt and Re from spent reforming catalyst by dissolution of the Al_2O_3 support, while leaving precious metals concentrated in the solid residue. Dissolution can be achieved by either H_2SO_4 or NaOH. The former is more suitable because it generates $Al_2(SO_4)_3$ as a sellable product. Seven patents were issued for recovery of the Pt from spent reforming catalysts using the support dissolution by H_2SO_4 between 1955 and 1974 [188]. This appears to be the most common procedure employed for recovery of the Pt and Re from spent reforming catalysts. The dissolution involves the following reactions:

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

In the acid medium, the Pt is unaffected while Re is solubilized producing a perrhenic acid, which can be removed from the solution using a solid ion exchange. Pt is then recovered from the solid as the chloroplatinic acid using an oxidizing chloride medium.

An example of the support dissolution method is the commercial process employed by Degussa in Germany [190]. In this process, the decoked catalyst containing Pt is treated with NaOH at a temperature of 200° and a pressure of 10 bar. During this treatment the support is converted to soluble sodium aluminate, which is then separated from the Pt by filtration. The Pt is converted to a soluble form by treating with HCl and Cl_2. Once in solution, Pt of at least 99.95% purity can be obtained. The Ir can also be recovered by using a similar method. Using this method, about 1000 ton of spent reforming catalysts are processed annually by Degussa.

The use of carbon as the support for various catalyst applications has been gaining importance. In this case, metal recovery from the spent reforming catalyst may also include removal of the support prior the metal recovery. According to the procedure described by Jacobsen [185], the spent catalyst is oxidized to remove deposited carry-overs. This follows by a prolonged burning of the carbon support, which usually lasts several days. After the removal of all carry-overs and carbon, the remaining material is more homogeneous. Also, its volume has been decreased substantially, usually by a factor of 3 to 10. A number of procedures is available for the final recovery of the metals in a pure form.

4.3.1.2. Dissolution of metals. Dissolution of metals using a mixture of HCl and an oxidant has been widely used for recovery of precious metals from automobile catalysts [188]. Oxidants such as HNO_3, NaOCl, HOCl, $NaClO_3$, $NaBrO_3$ and H_2O_2 can be used. The process can operate in a batch mode and a continuous mode. An NaCN solution was also used for dissolution of the precious metals.

Several procedures for recovery of Re and Pt from spent reforming catalysts were investigated by Mastny et al. [191]. The decoking of the catalyst was always the first step. The decoked catalyst was treated either with 5 M HCl/HNO_3 acids or ammonia. As it is shown in Fig. 44, decoking in the pure O_2 affected the solubility of Pt in HCl solution. The temperature had a significant effect on the solubility of Re and Pt (Fig. 45). Using the solution of HCl at 90°C, almost a complete dissolution of Pt and Re was achieved after the 2 and 4 h treatment, respectively. A complete dissolution of both metals was also achieved in the aqua regia but the necessary contact time was shorter. It is obvious from Fig. 45 that the effect of temperature can not be compensated by the contact time. In the other approach used by these authors, the decoked catalyst was also treated with the solution of a diluted ammonia at 60°C. After 1 h and 2 h of the treatment, 80 to 85% and 85 to 91% of Re, respectively was dissolved. Little effect on dissolution was observed by prolonging time of the treatment in the ammonia solution. Under these conditions, all Pt and about 10% of Re remain in the catalyst and can be recovered by using the acid treatment. Once the metals are in the solution, an efficient method has to be chosen for their recovery from the solution.

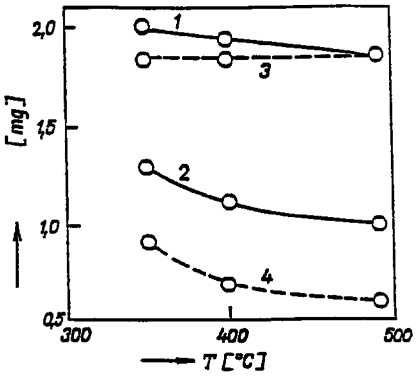

Fig. 44. Effect of temperature and oxidation conditions on solubility of Pt and Re [191]: 1, Re; 2, Pt oxidation in air; 3, Re; 4, Pt oxidation in oxygen.

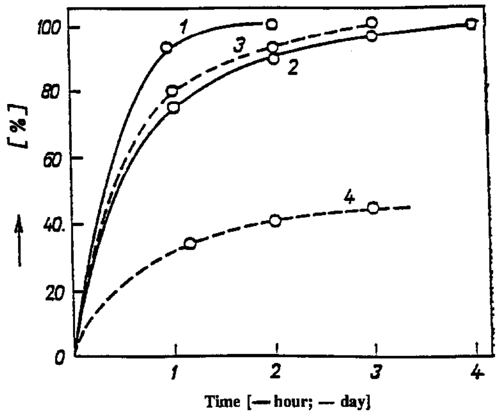

Fig. 45. Effect of temperature and time on solubility of Re and Pt [191]: 1, Re; 2, Pt at 90°C; 3, Re; 4, Pt at 20°C.

Tyson and Bautista [192] published a detailed study on the kinetics of the leaching of Pt and Pd from spent automobile catalysts using a mixture of HCl and HNO_3. It is believed that some observations and conclusions made during this study as well as the used approach are relevant for recovery of Pt and Pd from reforming cata-

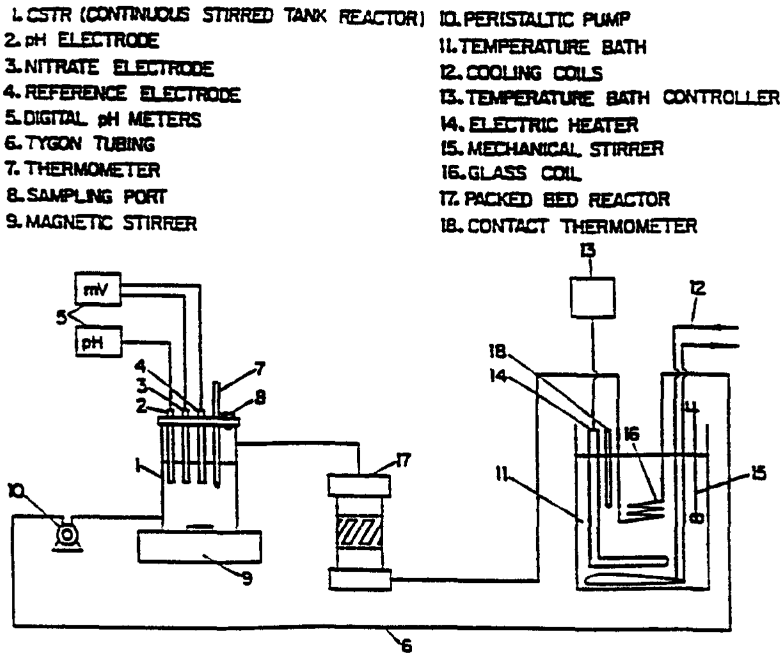

Fig. 46. Schematic diagram of the leaching equipment [192].

lysts. In view of the kinetic completeness of this study, it is felt appropriate to have its methodology and conclusions highlighted in the present review, even though it deals with the spent automotive catalysts. In this study, a honeycomb form of the catalyst was crushed to obtain 60 to 100 mesh particles. The schematic diagram of the experimental system is shown in

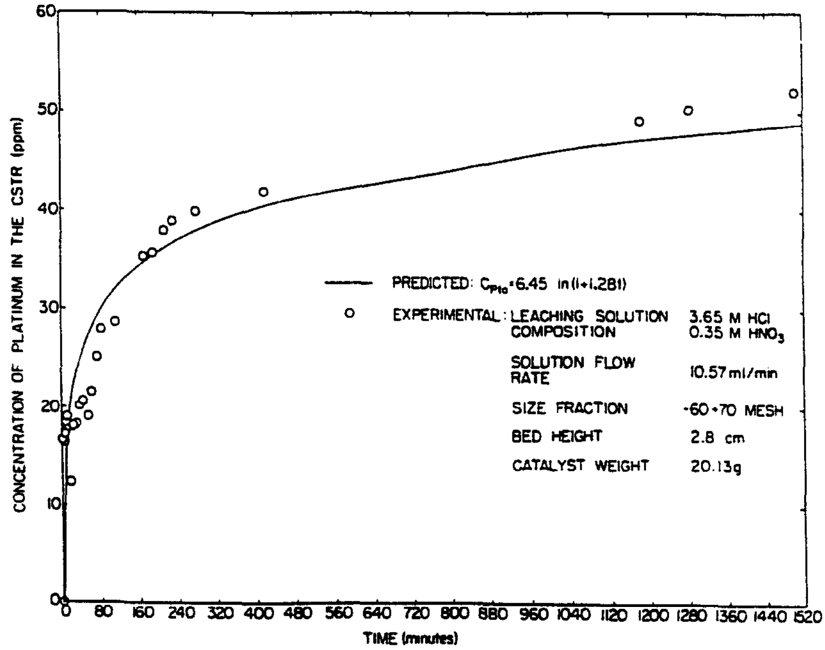

Fig. 47. Concentration of palladium in the CSTR versus time [192].

Fig. 46. It comprises a continuous stirred tank reactor (CSTR) and the packed bed reactor. Before every run, the CSTR was filled with 900 ml solution of 3.65 M HCl and 0.35 M HNO_3 and the packed bed filled with the catalyst. Then, electrodes were calibrated for various levels of NO^{3-} and H^+ ion concentrations. The pump was then turned on and the solution pumped through the fixed bed of the catalyst at 25°C before completing the loop back to the CSTR. At various times, electrode readings were recorded and samples of the solution taken for determination of Pt and Pd. The experimental results were used to fit different kinetic expressions. The best fit was obtained for the following expression:

$$C_{Ao} = A \ln(1 + Bt)$$

where A and B are empirical constants, t is time and C_{Ao} is the concentration of Pt and Pd at the exit of the CSTR. This equation appeared to fit the general shape of the experimental points such as those shown in Figs. 47 and 48, namely a rapidly rising concentration at the early stages, followed by a gradual levelling off at later stages. This equation also satisfied two boundary conditions, i.e. $C_{Ao} = 0$ and $dC_{Ao}/dt \rightarrow 0$ as $t \rightarrow \infty$. There were other equations which fit the points better but did not satisfy the boundary conditions and equations which satisfied the latter but did not fit the shape of the curve. It was observed that the rate of leaching decreased with increasing bed height, suggesting that the use of small multiple beds may be more efficient than to use one large bed. The concentration of Cl^- and NO_3^- ions influenced the relative rate of the leaching of Pt and Pd. Thus, when Cl^- concentration increased and that of NO_3^- decreased, the extent of Pd dissolution increased and that of Pt decreased. This indicates some difference between the mechanism of dissolution of Pt and Pd such as the redox reaction for the former and the dissolution of Pd to an ionic form. The particle size had little effect on dissolution of both Pt and Pd.

The US Bureau of Mines has tested an alkaline cyanide solution for the Pd recovery from three spent reforming catalysts [193]. These catalysts consisted of 0.4 to 0.7 Pd on a zeolite. During leaching, the catalyst exhibited ion exchange properties due to their zeolite matrices. This could present a safety hazard due to the potential for the HCN release. However, the catalyst leach residues passed the Federal TCLP

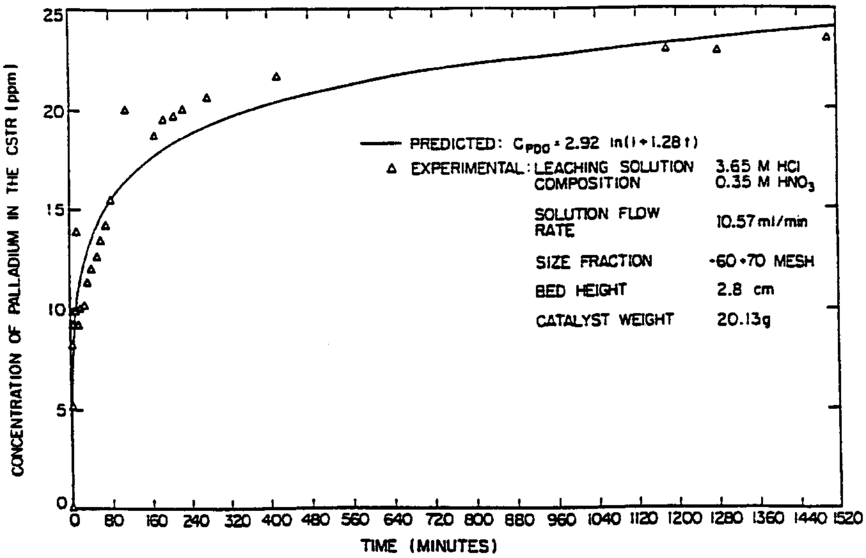

Fig. 48. Concentration of platinum in the CSTR versus time [192].

as well as the California Waste Extraction test, confirming that the landfill disposal of the leach residues would be environmentally acceptable.

L'Institut Francais du Petrole has disclosed a process for recovery of rhenium, which is subsequently reused for catalyst preparation [194]. In this process, the spent catalyst containing rhenium oxide deposited on porous alumina is heated in an atmosphere containing oxygen and treated with an oxygenated aqueous solution. The treated catalyst is then leached with an aqueous ammonia solution at pH > 12. The extract may be directly used for catalyst preparation.

4.3.1.3. Recovery of metals from solution. In every case a complete dissolution of metals in a solution is essential to ensure an efficient recovery. Once metals are in the solution, various extraction, precipitation and absorbtion procedures can be applied for their recovery.

Precipitation. It is claimed by Awadalla et al. [195] that this method is particularly suitable for recovery of Pt group metals from leach solutions from the acid leaching of the precious metals containing solids such as reforming catalysts. The method comprises the reduction–precipitation of the solution with sodium or potassium borohydride. The resulting precipitate is readily filtrable to give a high purity Pt group metals, whereas the barren solution can be recycled to the upstream process. In the process disclosed by Shell [196], the effluent containing Pd was contacted with a reducing agent and the resulted precipitate deposited on a combustible carbonaceous carrier, which was then separated from the effluent. The use of reductants such as Al, Zn and Cu metals to precipitate precious metals from chloride solutions is also reported [184].

Extraction. Mastny et al. [191] used two types of copolymer styrene-divinyl benzene for extraction of the metals from the solution, i.e. one containing sulphonic groups and the other trimethyl ammonium groups. A chloride form of the latter was used for the metal separation from the acidic solution. The anions such as $(PtCl_6)^{2-}$ and $(ReO_4)^-$ were adsorbed on the column, whereas the cations were not.

The separation of these anions was achieved by 1 to 5 M HCl which eluted Re anion followed by 5 M $HClO_4$, which eluted Pt-containing anions. In case of the acidic copolymer, all cations were adsorbed on the column whereas Pt- and Re-containing anions were not. The separation of these anions from the solution can be achieved using an OH^- form of the copolymer containing trimethyl amine group.

The separation of Pt from Rh contained in a solution could be enhanced by adjusting the oxidation and reduction potential of the solution to higher than 850 mV [197]. Subsequently, Pt can be extracted into organic solvent phase using tributyl-phosphate while Rh was isolated in the aqueous phase. Pt was back extracted from the organic solvent phase to the aqueous phase using a solution of hydrazine chloride.

Membrane separation. Li et al. [198] have compared the convection aided separation using chelating microporous membrane with the chelating-bead-packed bed for separation of Pd from a Pd chloride solution. The schematics of these systems are shown in Fig. 49. An iminodiacetate group was introduced on both the membrane and beads as the chelating agent. The Pd

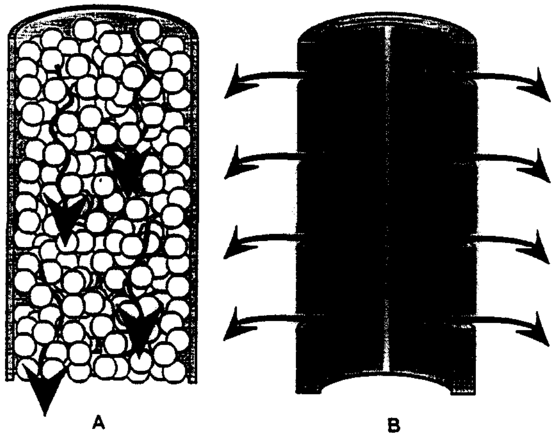

Fig. 49. Schematics of diffusion-limited separation (A) and convection-aided separation (B) [198].

was adsorbed by the agent, while the solution permeated through the membrane or the bead-packed bed. Subsequently, the adsorbed Pd was eluted by permeation of an HCl solution. A lower degree of tailing in the elution curve and a higher enrichment of Pd obtained on the chelating microporous membrane compared with the bead-packed bed, confirmed much better separation efficiency of the former. It is believed that this approach is also applicable to recovery of metals from the spent reforming catalysts, though so far, its potential for such applications has not yet been explored.

4.3.2. Other methods for recovery of precious metals

It is evident that the development of new or improved methods for recovery of Pt group metals has been attracting attention. The review of patent literature shows that before 1986 about 20 patents on recovery of Pt group metals from spent catalysts using different methods, were issued around the world [192].

Based on the information provided by Mishra [188], gas phase volatilization is another approach, which may be applicable to spent reforming catalysts. This method is based on the selective chlorination of Pt and Pd to form volatile products, which condense on cooling. Chlorine-containing agents such as $AlCl_3$, CCl_4, mixtures of $CO + Cl_2$ and phosgene can be used. Major constraints of this method is the handling of toxic agents and by-products.

Pyrometallurgical processes, such as plasma arc smelting, primary nickel smelting and secondary lead and copper smelting also have potential for the recovery of the precious metals from the spent reforming catalysts. In fact, it is concluded by Mishra [188] that a considerable advantage exists for nickel, copper and lead smelters in the recovery of Pt group metals from the catalysts.

An example of pyrometallurgical processes is the invention disclosed by the Japanese inventors [199]. This process comprises mixing the spent Pt containing catalyst with a mixture of copper and copper oxide and flux and reductant components. The melt of this mixture contained two layers, i.e. one containing Pt and metal copper and the other containing slag. These layers could be readily separated. The Pt containing mixture was heated in air to partially oxidize copper metal to copper oxide. This resulted in two layers, one containing the copper oxide and the other copper metal significantly enriched in Pt. These two layers could again be readily separated.

5. Conclusions

It is believed that general trends such as decreased availability of conventional crudes offset by increasing supply of heavy crudes will continue well into the next century. This will result in an increased consumption of hydroprocessing and FCC catalysts. This situation was summarized by Shelley [200] as follows: 'Petroleum refiners worldwide are struggling to comply with environmental mandates that tightly dictate the composition of transportation fuels. At the same time, many are trying to capitalize on cost advantages offered by heavy, dirty feedstocks. This is stimulating development of catalysts for residue cracking, hydroprocessing, isomerization and alkylation'. However, at one point, a thorough reevaluation of technologies may be necessary if the amount of spent catalysts and costs of their disposal and utilization will continue to rise. For example, residue cracking FCC units consume at least four times more catalysts than FCC units which process traditional gas oil feedstocks. Continuously increasing amounts of spent FCC catalysts which are more extensively contaminated than before, may change their current non-hazardous classification to that of hazardous solid wastes. One possible way to offset these trends is the development of more active and more metal tolerant catalysts for both FCC and hydroprocessing operations. The improvements which will have to be made to the current generation of refinery catalysts, to meet demands for further improvements in efficiency and environmental performance, was extensively discussed by Chianelli et al. [201].

The development of new catalysts is one of the alternatives to capital expenditures required to comply with environmental standards. In this regard, the reformulation of gasoline without compromising its quality may require new processing schemes. Of primary importance is the removal of aromatics from gasoline and offsetting the octane loss by increasing content of other high octane compounds. Oxygen addition to gasoline has been gaining on importance as well. In this regard, better catalysts will have to be developed for producing oxygenates such as MTBE, particularly for isobutylene required for production of MTBE. The trends from conventional to reformulated fuels will continue towards alternative fuels, involving a whole fuel replacement by alternative motor fuels such as alcohols and hydrogen. There are some reports that methanol and hydrogen are already being used in some parts of the world. The introduction of alternate fuels requires consideration of long term environmental effects. This, however, can only be answered once the performance of the alternate fuels is well understood compared with that of the conventional fuels. These developments require a coordinated approach involving refiners, motor vehicles manufacturers and environmental authorities.

The increasing importance of alkylation and isomerization processes is anticipated. Currently used acid catalysts will be gradually replaced by solid superacids with significantly diminished environmental risks. However, once such catalysts are commercial, procedures for their regeneration and handling will have to be established. Thus, the presence of halogens in these catalysts will still require some precautions to avoid risks entirely. Also, potential utilization schemes, after these catalysts can not be regenerated for reuse will need to be developed.

In the future, processing options which generate less or no hazardous wastes may be more acceptable, though at the present time, their costs may be prohibitive. For example, it was suggested that gasification of distillation residues is one of such options [202]. In this case, the residue is converted to synthesis gas which may be used for the production of several final products. At the same time, sulphur in the residue is also converted to a usable product. Other option may include residue upgrading by carbon withdrawal, such as coking to obtain additional distillates. The residual coke can be either combusted or gasified. The remaining ash/slag can be used for recovery of metals such as Ni and V [203]. These options offer almost no hazardous residues. It is noted that processes required for these options are all commercially available and have already been used for the combustion and gasification of coal as well as for the utilization of coal ashes and slags. Modifications and improvements in these technologies to suit refinery residues have been attracting attention. Currently, there are several projects in the design stage and/or under construction around the world, considering refinery residues as primary feedstocks. Novel technologies are also being developed.

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