Tetronics

Whitepaper

Recovery of Ruthenium and other PGMs from Spent Petrochemical Catalysts

Case Study:

Recovery of Ruthenium and Other PGMs from Spent Petrochemical Catalysts

The recovery of platinum group metals from spent petrochemical catalysts has economic benefits by the protection of the supply chain of these valuable and rare metals, thereby helping to create a sustainable value chain in the petrochemical industry for catalysts.

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Introduction

The platinum group metals (PGMs) are used extensively in catalysts for the petrochemical industry owing to their excellent catalytic properties. Their high value and natural scarcity mean that high recycling rates not only have economic benefits but also environmental benefits, thereby generating a sustainable supply of these metals. Thermal plasma is a pyrometallurgical technique which is used extensively for the recovery of the PGMs from catalysts and recovery efficiencies of over 98% can be achieved. This paper outlines the use of thermal plasma in the recovery of these metals from petrochemical catalysts with a case study of Tetronics plasma facility recovering ruthenium from spent petrochemical catalysts.

Platinum Group Metals in the Petrochemical Industry

Despite their scarcity, the catalytic properties of the PGMs make them especially important for industrial use, particularly in petrochemical catalysts. The use of PGMs in petrochemical catalysts has been well established for decades and are used widely in reformation, hydrocracking and isomerisation processes.

Platinum and palladium are the most widely used PGMs in petrochemical catalysts although they are often used in combination with other PGMs and occasionally other metals such as rhenium and cobalt. These additions can enhance the stability of the catalysts; rhenium for example is added to Pt/Al_2O_3 catalysts to maintain the catalyst's activity under high level of coking as well as enhancing its selectivity in the reforming of naphtha.

Bifunctional catalysts such as Pt/Ca-Y-zeolite catalysts are used in the hydrocracking process. The Pt allows for the dehydrogenation of reactants to alkenes and the hydrogenation of olefins whilst the zeolite component acts as a Brønsted acid site which cracks the feedstock into intermediates for dehydrogenation/hydrogenation.

Table 1: Examples of PGM containing petrochemical catalysts

Petrochemical Application	**Precious metals**	**Precious metal loading (wt%)**	**Catalyst Support**
Isomerisation	Pt	0.5	Y-zeolite (SiO_2-Al_2O_3-Na_2O)
Reformation	Pt, Re	0.4, 0.3	Al_2O_3
Hydrocracking	Pt	0.5	SAPO-11 (SiO_2-Al_2O_3-Na_2O)
H_2S capture	Ru	1.7	Al_2O_3-TiO_2
Gas to liquid	Pd	0.4	Al_2O_3-SiO_2-TiO_2

The advantage of PGMs is that the reactants are adsorbed with a moderate strength compared to base metal catalysts. This means that the process reaction rates are favourable, whereas either a too strong or a too weak adsorption strength causes a slow reaction rate which is less commercially attractive. Therefore, although alternative non-PGM catalysts do exist, the PGM catalysts remain trusted and effective and are ultimately difficult to replace.

Examples of PGM bearing catalysts are shown in Table 1 and it can be seen that the typical loading of PGMs on catalysts ranges from 0.2 wt% to over 1 wt%. A loading of 0.3 wt% is around 400 times greater than the PGM concentration in their primary ores and the high value of these metals coupled with their natural scarcity mean that spent catalysts are an important secondary source of PGMs. This has stimulated high recycling rates of spent catalyst in the petrochemical industry, which operates as a semi-closed loop recycling market where the precious metals are recovered and reused and the only requirement for virgin metal is to cover losses from the system due to use and recycling losses (Figure 1).

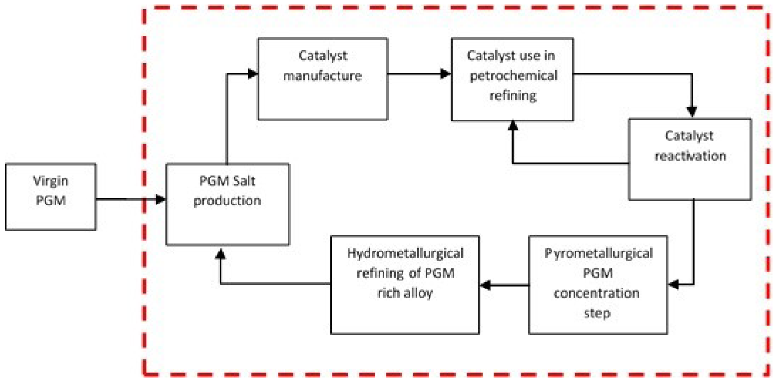
PGM Recovery Processes

The recovery processes for these metals can be broadly divided into two major types: hydrometallurgical and pyrometallurgical routes.

The hydrometallurgical routes rely on wet chemistry extraction and precipitation techniques. For example the catalysts undergo a pre-treatment stage to dissolve the catalytic support and the then the noble metals can be leached using a suitable lixiviant such as aqua regia or sulphuric acid depending on the selectivity required or chemistry of the metals. The target metals are then precipitated as salts which can be then purified using a roasting process, if required.

Pyrometallurgical processes are thermally based treatment techniques where the catalysts are treated at high temperatures thereby melting the components. The ceramic-like supports of the catalysts form a slag material which has a lower density than the metallic components which are then able to move through and settle beneath the slag and be separated. The addition of a collector metal is often required due to the small particle size of the metallic particles which inhibits their settling rate through the slag. The collector metal forms larger particles which settle through the slag at a faster rate and absorb the target metals forming an alloy. This alloy is rich in the target metals and is then sent for subsequent refining, usually via hydrometallurgical routes.

Figure 1: The petrochemical semi-closed loop PGM recycling market



It is often practical to utilise a combination of pyro and hydrometallurgical routes to achieve maximum recovery efficiencies of the PGMs. The hydrometallurgical processes are often very sensitive to compositional variation in the feedstock and can experience difficulties in directly processing spent catalysts due to the high stability of the catalytic support. A particular issue is found with Al_2O_3 supports where the PGMs are originally seeded onto a γ-Al_2O_3 support, the metastable phase of alumina, which under the petrochemical process conditions can undergo a phase change to α-Al_2O_3 which is extremely difficult to dissolve and so results in significant recovery losses. Consequently hydrometallurgical recovery rates can vary from 85% to 95%.

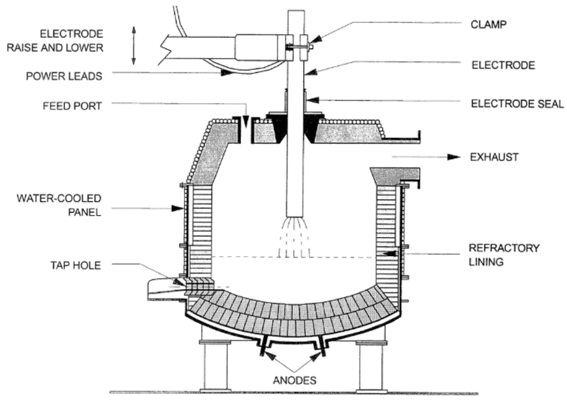
Pyrometallurgical routes on the other hand are not so sensitive to variations in the composition of the feed material or the phase of the support and are able to treat a large volume of material at high throughputs. Difficulties in pyrometallurgical processes can arise when there are metallic components which have high vapour pressures or are easily oxidised meaning that they can be vaporised and the process requires off gas capture of these metals which can become quite complex. The pyrometallurgical processes often require the use of hydrometallurgical routes for the final refining of the alloy produced, which is often iron or copper based; however this is much more suitable for final refining than the original catalysts and so high recovery rates can be achieved.

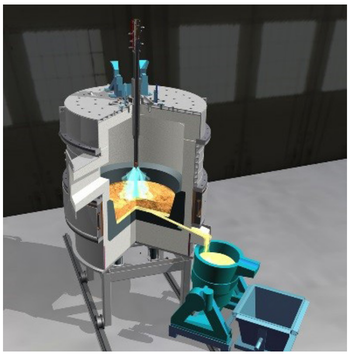
This paper will now focus on the use of thermal plasma arc furnaces, which is one such pyrometallurgical technique used extensively in industry for the recovery of valuable metals from spent catalysts and other wastes and ores. These plasma processes are typically able to achieve high recovery efficiencies of PGMs from catalysts of over 98%.

Thermal Plasma Technology

Tetronics is a world leader in thermal plasma technology, which has been used in a range of industrial applications, for example in the tundish plasma heating where the technology is used to control steel temperature when superheating steel to improve its quality. It is also used for the treatment of hazardous materials such as air pollution control residues, asbestos and intermediate nuclear waste where the hazardous materials are vitrified into a non-hazardous, non-leaching glass.

Figure 2: Thermal plasma furnaces





Plasma is formed from the ionisation of a gas using electrical energy. Under specific conditions, the 'plasma arc' which is formed is of very high temperatures, typically over 5000 K, and so can be used as an intense heat source. Consequently thermal plasma is also widely used in smelting applications and in particular for the recovery of valuable metals from spent automotive and industrial catalysts. The recovery of PGMs from catalysts is well established and Tetronics installed PGM recycling plants in Asia, Europe and USA which have a combined PGM recycling capacity of 1.2 million troy oz per year with the typical throughput of a plasma PGM recycling facility being 1,500 to 3,000 tonnes per year of catalysts. Examples of Tetronics' commercial plants can be seen in Table 2.

Table 2: Examples of Tetronics commercially installed plasma processing plants

Business Area	Plasma Process	Customer and Country	Through-put	Process Description
Environmental (treatment of hazardous waste)	Vitrification of incineration ashes.	Mitsubishi Heavy Industries, Japan	25,000	Ashes from the incineration of municipal solid waste are vitrified into a safe non-leaching glass which suitable for use as a product.
Metal Recovery	Recovery of stainless steel electric arc furnace dust.	Outokumpu Stainless Melting and Continuous Casting, UK	8,000	EAFD fed into plasma chamber to recover ferroalloy containing chromium and removing hazardous lead and zinc from the dust.
Metal Recovery	PGM recovery from spent autocatalysts and industrial catalysts.	Heesung PM Tech, Korea	3,500	PGM rich alloy is produced via plasma smelting of spent catalysts. The PGM alloy is suitable for final hydrometallurgical refining.
Metal Recovery	PGM recovery from spent petrochemical catalysts.	Furuya Metals, Japan	1,000	Ruthenium rich alloy produced from the plasma smelting of spent petrochemical catalyst.
Metal Recovery	PGM recovery from spent petrochemical catalysts.	Russian client	1,850	Platinum and rhenium rich alloy produced from plasma smelting of spent petrochemical catalysts.
Metal Recovery	Electronics waste smelting plant	BlueOak, USA	7,000	Valuable metals such as gold, palladium and silver recovered from electronic waste into alloy suitable for refining.

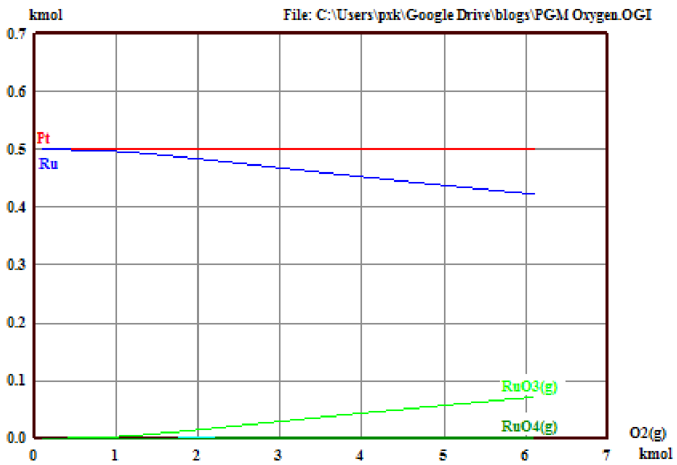
A thermal plasma furnace consists of a refractory lined steel vessel which has water cooled roof and upper sections (Figure 2). The plasma is generated by passing a gas, usually nitrogen or argon, through a hollow tubular device which can be either a graphite electrode or a water-cooled plasma torch. The gas is excited using electricity where it becomes ionised and forms a plasma arc. In the metal recovery process, the catalysts which are to be treated are blended with fluxing agents and slag makers to reduce the overall melting temperature of the feed material and to improve process dynamics i.e. the viscosity of the melt. Once blended, the feedstock is fed into the plasma furnace where it is melted by the plasma arc.

The molten material in the furnace acts as an anode and the arc is transferred between the electrode (which acts as the cathode) and the melt completing the electrical circuit; this is known as a transferred arc operation. The electrode is able to be manipulated to more effectively distribute the energy across the molten material inside the furnace in order to maximise the melting and recovery of the valuable metals.

As the feed material is melted, a metal phase, a slag phase and a gaseous phase are produced. The metal phase settles beneath the less dense slag phase and the gaseous products are removed from the furnace and pass through a gas treatment facility. The gas treatment facility consists of a number of process units to ensure that the emissions to air are compliant with regulations.

The advantages of thermal plasma in the recovery of the PGMs from materials like catalysts include the excellent PGM recovery rates, the small footprint of the processing plant and also, importantly, the tight control over the process conditions which makes the process flexible to suit the specific chemistry of the target materials. This is important for the processing of materials which may be oxidised easily and which have high vapour pressures. Under high temperatures this could lead to losses of the metals, instead because a plasma arc is generated by electricity, the conditions inside the furnace can be controlled tightly and the oxidation of these metals minimised as no fuels or oxygen are required to maintain heat, in contrast to combustion processes.

Figure 3: Thermodynamic model (using HSC software) showing the behaviour of Pt and Ru at 1500 °C



Platinum, palladium and rhodium are not easily oxidised at high temperatures; however some PGMs such as ruthenium can be oxidised and also other components on bi-metallic catalysts such as rhenium. Figure 3 shows the behaviour of platinum and ruthenium at 1500 °C under increasing oxygen concentrations and it can be seen how Pt does not become oxidised whereas ruthenium does and these oxides are gaseous species. To recover the ruthenium to the alloy phase reducing conditions need to be maintained in the furnace, the flexibility of the plasma furnace operation means that these can be maintained closely and in order to maximise the recovery of these metals.

Case Study:
Ruthenium Recovery from H_2S Abatement Catalysts

Tetronics has installed a plasma plant at Furuya Metals in Japan (Figure 4) which treats ruthenium bearing petrochemical catalysts. These catalysts are derived from the petrochemical industry and are used for the removal of H_2S from gaseous streams in the refining process. The plant was commissioned in 2013 and has been in operation with a throughput of 1,000 tonnes per year of catalysts.

Figure 4: Tetronics plasma processing system as Furuya Metals in Japan

Looking specifically at the ruthenium catalysts, the ruthenium is impregnated onto a support comprised of aluminium oxide (Al_2O_3) and titanium dioxide (TiO_2) and the concentration of the ruthenium on these catalyst is 1.8 wt%. To reduce the melting temperature of the input feed, the catalysts are blended with lime (CaO) and silica (SiO_2) and so Al_2O_3, TiO_2, SiO_2 and CaO are the major slag components in the system. The slag produced in the process is a vitrified material known as Plasmarok® which is suitable to be used as a product in further applications for example as an aggregate.

Iron is used as the collector metal in the process and is added as magnetite (Fe_3O_4) which is reduced using coke. The addition of coke helps to maintain the reducing conditions required in the process to maximise the recovery of ruthenium as does the generation of CO via the reduction of magnetite.

The ruthenium is recovered as an iron alloy where its concertation is around 5 wt% in the final alloy. This alloy is able to be further refined, usually using hydrometallurgical processes, to recover ruthenium to the desired purity. Recovery efficiencies of 98% of ruthenium are achieved during the plasma smelting stage. The ruthenium rich alloy produced in the process generates economic benefits to Furuya, which is a process credit of approximately $2m per year.

Conclusions

The recovery of platinum group metals from spent petrochemical catalysts has economic benefits by the protection of the supply chain of these valuable and rare metals, thereby helping to create a sustainable value chain in the petrochemical industry for catalysts.

The flexibility of the operation of a thermal plasma furnace means that the processing of a wide range of metals, not just noble metals, can be achieved. The combination of pyrometallurgical techniques such as thermal plasma smelting systems to produce a PGM rich alloy with final refining via hydrometallurgical routes enhances the recovery of these valuable metals. This enables the closed loop recycling market to be enhanced in the petrochemical catalyst industry with minimal losses from recycling. The use of PGMs in the petrochemical industry is not forecasted to diminish and so enhancing the recycling rates of these rare and valuable metals increases the sustainability and self-sufficiency of their supply.

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