# RECOVERY OF VALUABLE BASE METALS FROM SECONDARY MATERIALS USING DC PLASMA SMELTING

T. P. Johnson[1]

*[1]Tetronics International*
*Marston Gate*
*South Marston Park, Swindon, Wiltshire, UK SN3 4DE*
*(tim.johnson@tetronics.com)*

## ABSTRACT

The increasing use of nickel, cobalt and other valuable base metals as lower-cost alternative catalyst materials, increasing stainless steel production and the potential for increased demand in a range of other applications has resulted in strong growth in demand for these key metals. However, against this growing demand, mining companies face a combination of persistent low metal prices, increasing costs of primary extraction and declining quality of ores, conditions that make it the ideal time to recover more nickel, cobalt and other key metals from secondary sources. For more than 25 years, Tetronics' DC plasma smelting technology has proved itself to be very adept at extracting nickel and other key metals such as chromium and molybdenum from stainless steel melt shop dusts and other wastes. The highly compact, environmentally friendly and efficient nature of Tetronics' DC plasma smelting plants makes them an obvious choice for these increasingly important niche secondary sources of nickel, cobalt and other key metals. So, as the world looks for new environmentally-friendly methods to satisfy the growing demand for these metals, this paper will present details of how Tetronics' DC plasma smelting technology can be used for their recovery from secondary sources.

## KEYWORDS

Plasma, Plasma smelting, Catalysts, Metal recovery

# INTRODUCTION

Valuable base metals, such as nickel, cobalt, molybdenum, vanadium and tungsten, are used in a wide range of important technological applications. The demand for many of these metals has increased significantly over the last few decades, driven especially by economic expansion in Asia generally and China in particular. This has led in turn to a large growth in the output of mines in order to satisfy this increasing demand, as shown by the data in Table 1 (USGS, 1994, 2014). These data reflect an even longer trend of growth of these metals, with nickel, for example, showing an average rate of 5.3 % per year from 1980 until 2015 (International Nickel Study Group, 2017). This rapid and sustained rate of growth means that annual mine outputs for nickel, tungsten, molybdenum and vanadium have had to double roughly every 11 to 14 years, whilst cobalt mine output has had to double roughly every 7 years, over the period from 1994 until 2014. With the average working life of a nickel mine being between 17 and 22 years (Statista, 2017), this means that from the time a nickel mine opens until it closes, the industry needs to find the equivalent of another three or four mines of a similar output to satisfy this relentless growth in demand for the metal.

Table 1. Annual mine production for several key base metals (USGS, 1994, 2013)

| Metal | Mine Production (tonnes per year) | | Annual Growth (%) |
| --- | --- | --- | --- |
| | 1994 | 2013 | |
| Copper | 9,430,000 | 18,200,000 | 3.5% |
| Nickel | 895,000 | 2,660,000 | 5.9% |
| Molybdenum | 104,000 | 268,000 | 5.1% |
| Cobalt | 18,500 | 123,000 | 10.5% |
| Tungsten | 25,500 | 83,300 | 6.4% |
| Vanadium | 34,300 | 80,400 | 4.6% |

In the face of such a growth in mine output, it is perhaps not surprising that ore grades have been declining and the energy costs of extraction have been increasing in response. For example, in the case of copper mining, where the growth in demand has not been as steep as with the other metals shown in Table 1, the average ore grade has gone down by 25 % in just ten years whilst the energy consumption per tonne of production has increased by around 12 % (Calvo, Mudd, Valero & Valero, 2016).

These same pressures on demand, coupled with a growth in commodities prices and increasing costs of primary production, create the perfect conditions to drive an increase in recycling rates. This is reflected in data that show the proportion of total nickel supply in the USA being recycled grew from 35 % in 1994 to 45 % some ten years later (USGS, 1996, 2006). However, there has been essentially no increase in this rate of recycling in the last ten years, with nickel recycling rates in the USA remaining around 45 % (USGS, 2016), whilst recycling rates globally remain even lower than this (International Nickel Study Group, 2017). There is, therefore, a clear need within the industry for further increases in recycling of all valuable base metals from secondary sources in order to reduce the pressure on primary supply. In particular, there is a need for technologies that will address the secondary materials outside of stainless steel and other similar metallic sources of the key valuable base metals that have reasonably well-established recycling routes.

## SECONDARY SOURCES OF NICKEL & COBALT

There are a range of 'non-metallic' secondary sources of these valuable base metals, including electroplating residues, batteries and so forth. However, some of the most interesting arise from the petrochemical industries and especially in catalysts. The use of these metals as catalysts has been known for over a century and although they were displaced somewhat by the use of platinum in the mid-20th Century, they are increasingly important as lower-cost alternatives in several important reactions, including the hydrogenation of vegetable oils, reforming of hydrocarbons, and the production of fertilizers, pesticides, and fungicides. Typical base metal contents of several different spent catalysts, including hydro-desulphurisation (HDS) and hydrocracking (HS) catalysts, are given in Table 2. These data show

just what a rich source of base metals these catalysts are, compared with the increasingly poor quality of ores.

Table 2. Typical spent base metal catalyst compositions, calcined basis (wt%)
([1]Scherzer & Gruia, 1996; [2]Canham & Aurich, 1991; [3]Johnson, 2017)

| Element | NiMo[1] | CoMo[1] | NiW[1] | HDS[2] | HC[2] | HDS[3] |
|---------|---------|---------|--------|--------|-------|--------|
| Ni | 2.6 | 3.1 | 2.5 | 2-3 | 3-4 | 4.2 |
| V | 0.05 | 10.5 | <0.04 | | | 0.7 |
| Co | <0.04 | 2.1 | <0.05 | 2-3 | 3-4 | 1.1 |
| Mo | 12.3 | 6.2 | 0.5 | 4-9 | | 11.0 |
| W | <0.05 | <0.05 | 15.2 | | 10-12 | |

In addition, crude oils typically contain small amounts of Ni, Mo and V that can become concentrated in various forms of refinery residues; these provide another potential petrochemical industry-based source of valuable base metals for recovery purposes.

## DC PLASMA ARC TECHNOLOGY

Ni, Co, Mo and other valuable base metals have been recovered from a wide range of sources using various hydrometallurgical and pyrometallurgical methods. These methods include DC plasma smelting (Canham & Aurich, 1991; Scherzer & Gruia, 1996), roasting with Na salts followed by either neutral leaching and alkali digestion (Marafi, Ran & Al-Sheeha, 2014) or acid leaching (Sivasakthi & Sathaiyan, 2012), and acid leaching and chelation (Oza & Patel, 2012).

Tetronics' DC Plasma Arc technology is one of several pyrometallurgical solutions available for the recovery of valuable base metals from secondary sources, the other key ones being shaft furnace and submerged arc furnace smelting. Shaft furnaces and submerged arc furnaces are both typically used at tonnages of more than 10,000 tonnes per month of alloy output (Barker, 2011), which is likely to be an order of magnitude larger than the typical furnace output that could be justified by spent catalyst availability. Submerged arc furnaces are commonly used in the ferroalloy industry and can sometimes accept calcined catalyst as an input alongside their main raw materials, but this is unlikely to be an approach that provides an economically or environmentally acceptable outcome in many cases.

By contrast, Tetronics' DC plasma smelting technology is ideally suited to operating at these lower annual tonnages as a result of the greater arc stability provided by the plasma. Tetronics' DC plasma smelting technology has been used commercially to recover Ni, Cr, Mo, Mn and Fe from stainless steel dusts since 1989 (Cooke & Roddis, 1989; Johnson & Deegan, 2012), in one case leading to the realisation of $190 million of value from these wastes over a 20-year period (Johnson & Makepeace, 2013). Tetronics' DC plasma arc technology has also been used for the commercial recovery of platinum group metals (PGM) from automotive and industrial catalysts for over 30 years. The unique combination of design and operational benefits of the technology during this period has ensured that industry-leading technical recovery rates have been demonstrated for a wide range of precious metals (PM) and PGM at both a pilot and full commercial scale (Johnson, 2016). These recovery rates are typically around 98 to 99 % for all major PM and PGM in spent automotive catalysts (typically cordierite-based) and petrochemical catalysts (typically alumina-based). More recently, the technology has been applied commercially to the recovery of PM/PGM from printed circuit boards (Johnson, Deegan & Wise, 2012).

This is because of several key features, including its ability to operate with a wide range of feed materials, tight control of smelting conditions and minimal losses of dust to the exhaust gases as a result of the low gas flows associated typically with DC plasma arc-based processes. The high furnace temperatures and the ability to vary the reaction conditions of the process also allow the operator to separate the elements in the charge into gaseous, slag and metal fractions. This in turn maximises the value derived from the waste and minimises the secondary waste arising, whilst achieving low ultimate emissions to air and water.

**Process & Plant Description**

In a typical DC plasma metals recovery plant (see Figure 1), the input material is conditioned as required.  In the case of petrochemical catalysts, it is highly likely this will involve a calcining or roasting step, to remove the residual levels of sulphur and organic residues from the refining processes in which they were used, although other operations such as crushing may also be required. The prepared material is then blended with various additions as required.  These additions can include fluxes (typically calcia and/or silica) to adjust the melting point and viscosity of the slag, plus reducing agents to aid recovery of reducible metals from the input material.  It is also possible to add steel scrap in order to adjust the final alloy composition if required.  The charge materials are then fed into the furnace via one or more feed ports in the furnace roof.
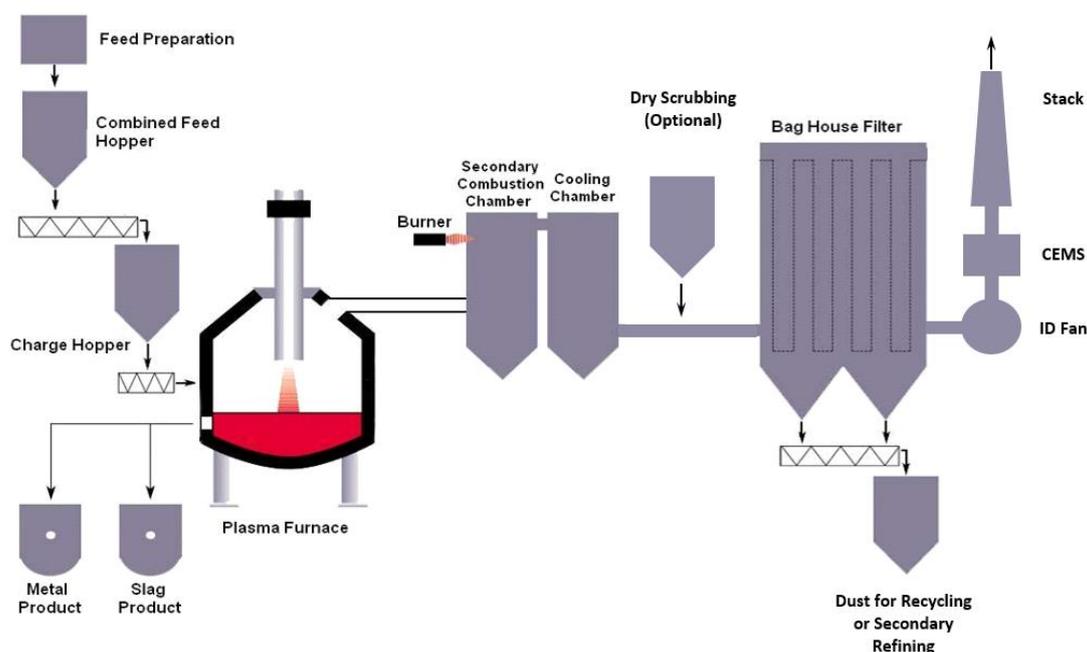
Figure 1. Schematic process flow diagram for a typical DC plasma smelting plant

The plasma furnace (see Figure 2) consists of a refractory lined steel vessel, which is water cooled in the roof and upper shell areas, and with either a graphite electrode or a water cooled plasma torch as the plasma device, which is inserted through the furnace roof.   The electrode is hollow to allow the optional flow of a small amount of stabilizing plasma gas, usually nitrogen.  Electrical power for the arc is provided by the plasma power supply, which converts the incoming AC voltage supply into the controlled DC supply required for the plasma; as with normal polarity welding, the molten bath is usually the anode of the circuit and the graphite electrode or plasma torch is usually the cathode.  The plasma arc attaches onto the surface of a molten bath of slag, which floats on a layer of liquid metal in the bottom of the plasma furnace, both of which are typically at a temperature of 1300–1600 °C, depending on the melting point of the materials.  The charge material feed falls onto the molten slag bath, which causes the moisture and volatile species (e.g. organics, volatile metals and metal halides) to vaporize; these are drawn off into the exhaust gases at around 1000–1200 °C before exiting to the gas cleaning system.

The gases from the outlet of the furnace pass into a secondary combustion chamber, which oxidizes flammable species such as persistent organic compounds and volatile metals.  The combusted off-gas is cooled to below 200 °C using either air or water injection to prevent reformation of dioxins and

furans. The cooled gas then passes through a filter unit to remove particulates.  A small proportion of the blended feed is carried over into the exhaust gas and is collected in the filter for disposal, sale, refining or recycling back in the plasma furnace, depending on its composition.  The removal of acid gases can be accomplished by the injection of hydrated lime into the gas stream upstream of the filter unit or via a wet scrubber after the filter unit, depending on the application.  The pressure inside the plasma furnace is carefully controlled to be just below atmospheric pressure by means of a variable speed, induced-draught fan, which prevents significant ingress of air or egress of process gases.  The exhaust gas is analysed and logged in accordance with local environmental regulations, typically using a continuous emissions monitoring system (CEMS), before being vented to atmosphere.
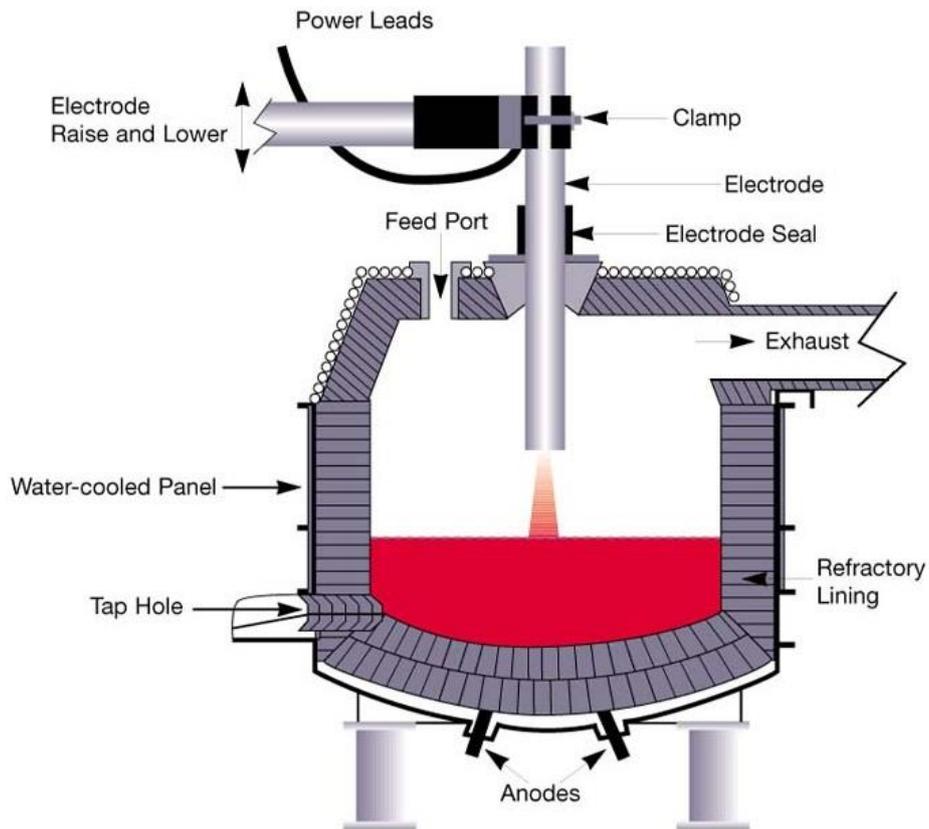


Figure 2. Schematic diagram of a plasma furnace

The petrochemical catalysts shown in Table 2 consist typically of metal oxides on an alumina substrate.  This substrate material makes these catalysts less amenable to many recovery methods than metallic sources of the metals, such as stainless steel and alloy steel scrap, which can be readily recycled directly into steel making operations.  Meanwhile, other methods (often based on various types of wet chemistry) also have significant drawbacks, such as poor recovery rates or the generation of large quantities of other wastes.

By contrast, not only has Tetronics' DC plasma smelting technology proved itself to be very adept at extracting nickel and other key metals such as chromium and molybdenum from dusts generated in the melting and production of stainless steel over many years, it has also been used for extracting precious metals from both alumina-based industrial catalysts and cordierite-based automotive catalysts.  As the use of base metals in catalysts for chemical processes is expanding, so these two strands of Tetronics'

experience come together to provide a compact, environmentally friendly and efficient method for the recovery of nickel and other base metals from petrochemical catalysts.

**Operating Requirements**

The feed blend and other key operating parameters are shown in Table 3 for one potential HDS catalyst with a composition based on data shown in Table 2 (Johnson, 2017).

Table 3. Key operating parameters for plasma smelting of example HDS catalyst

| Parameter | Per tonne blended feed |
|---|---|
| HDS catalyst | 565 kg |
| Flux, CaO + SiO$_2$ | 315 kg |
| Reductant, met coke | 50 kg |
| Steel scrap | 80 kg |
| Gross energy | 1,000 kWh |
| Slag produced | 710 kg |
| Alloy produced | 180 kg |

Similar parameters for the plasma smelting of stainless steel dusts and alumina-based PGM catalysts are provided in Table 4.

Table 4. Key operating parameters (per tonne blended feed) for plasma smelting of stainless steel dusts and PGM-containing alumina catalysts

| Parameter | Stainless Steel Dusts | PGM-Alumina Catalysts |
|---|---|---|
| Stainless steel dusts, catalyst | 790 kg | 360 kg |
| Flux, CaO + SiO$_2$ | 40 kg | 565 kg |
| Reductant, met coke | 170 kg | 25 kg |
| Gross energy | 1,520 kWh | 1,510 kWh |
| Slag produced | 310 kg | 900 kg |
| Alloy produced | 230 kg | 50 kg |

These data show that in many respects the conditions required for plasma smelting of HDS catalysts lie between these two other applications, which provide good reference points for the smelting of the base metal catalysts.

In terms of bulk composition, HDS catalysts are closer to the alumina-based PGM catalysts. This is because stainless steel dusts and other melt shop wastes tends to be a mixture of oxides that requires much less fluxing than either the base metal or PGM-based chemical catalysts that have an alumina substrate. This also leads to the alumina-based catalyst materials producing significantly higher amounts of slag than stainless steel dusts. Similarly, stainless steel dusts contain significant amounts of chromium oxide, which require very reducing conditions to extract the Cr as a ferrochrome alloy and this in turn increases the carbon addition required compared with the catalyst-based materials. In the case of the HDS catalyst, the target metals (Ni, Co, Mo, etc.) are all more easily reduced than Cr, and in the case of the PGM-containing catalyst, iron oxide is added as a source of collector metal, which is also more easily reduced and therefore both catalyst-based materials require smaller additions of carbon.

One area of difference lies in the gross energy requirement, which is significantly lower for HDS catalyst than for either of the other two examples. Another consequence of the more reducing conditions required for smelting the stainless steel dusts is that the net energy requirement tends to be higher with stainless steel dusts than for the catalyst-based materials. However, stainless steel dusts and HDS catalysts are processed typically at a much larger scale than PGM-containing chemical catalysts, with typical plant capacities being 10,000–40,000 tonnes per year and 1,000–2,000 tonnes per year respectively. The smaller PGM recovery furnaces tend to achieve a lower thermal efficiency than the bigger base metal recovery

furnaces and therefore the overall gross energy requirement for PGM-containing chemical catalysts tends to be similar to stainless steel dust processing. In the case of HDS catalyst, the combination of the higher efficiency achieved by the larger furnace size and the lower net energy requirement from the more easily reducible oxides results in a lower gross energy requirement than either of the two other examples.

**Process Outputs**

In the HDS catalyst plasma smelting example given above, the expected alloy composition is shown in Table 5. As can be seen from Table 2, Mo is often (as in the example used here) the major base metal used in the catalyst. Mo has a high melting point (2,623 °C) and therefore it is sometimes useful to add a source of Fe, for example in the form of scrap steel, so that the Mo content is low enough to give a melting point of less than 1,500 °C. This enables the furnace operating temperature to be limited to the capability of standard refractory linings.

Table 5. Expected metal alloy composition from HDS catalyst example

| Metal | Content (wt%) |
| --- | --- |
| Fe | 46.6 |
| Mo | 33.4 |
| Ni | 12.6 |
| Co | 3.4 |
| P | 1.8 |
| C | 2.0 |

It can also be seen from Table 5 that the alloy may contain residual amounts of P, depending on the composition the calcined catalyst, plus a level of C as well. There are typically strict limits on the P content of ferroalloys and therefore it is likely that some additional post-smelting process will be required to remove the P and C to achieve acceptable levels in the final alloy. Removal of the P can be achieved by either an oxidative process or a reductive process (Sano & Katayama, 1992), but because of the need to remove C as well, it seems likely that an oxidative process will be preferable. In this case, the standard approach is to use an oxidising slag containing CaO and FeO to remove the P, whilst a process such as argon oxygen decarburisation (AOD) could be used to remove the C.

## CONCLUSIONS

Rising demand for Ni, Co and other valuable base metals over recent decades has led to a doubling of primary output of these metals every 11–15 years or so, which in turn has resulted in a corresponding decrease in ore quality and an increase in mining costs. Despite this, recycling rates for some of these metals has remained static for many years. Consequently, non-metallic secondary sources of Ni, Co, Mo, V, W, etc., such as base metal petrochemical catalysts, have been attracting greater attention as potential targets for recycling. These materials often present challenges to existing recovery methods and DC plasma smelting provides a well-established alternative extraction route.

Tetronics' DC plasma smelting technology has been used for many years at both pilot and commercial scale for the recovery of base metals from a wide range of materials and stainless steel plant wastes in particular, and for the recovery of PGM from alumina-based petrochemical catalysts. This experience makes DC plasma smelting an ideal method for the extraction of Ni, Co, Mo and other valuable base metals from these alumina-based petrochemical catalysts.

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