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The recovery mechanism of platinum group metals from catalytic converters in spent automotive exhaust systems

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Abstract

The recovery of platinum group metals (PGMs) from catalytic converters of spent exhaust systems is considered in this paper. To be cost-effective, recovery processes must be well over 90% efficient and so the optimisation of their operation is vital. Effective optimisation requires a sound understanding of the operation and the underlying process mechanisms. This paper focuses on pyrometallurgical recovery operations used and typified by the Johnson–Matthey process. Analysis of this process reveals that it cannot be simply explained by the gravity model that is normally assumed. The analysis reveals that the affinity of PGM particles for the melted collector metal is a key factor in the behaviour of the process. A rational explanation of the key issues that govern the process behaviour is proposed and shown to be consistent with available operational data. The results generated would be applicable to other similar processes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Platinum group metals; Recovery mechanism; Catalytic converters

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1. Introduction

Automotive catalytic converters have been used increasingly since the mid-1970s in the USA (and more recently around the world) to meet emission limits enforced by international legislation [1]. The catalysts contain either platinum or platinum/palladium combinations to convert carbon monoxide and hydrocarbons to carbon dioxide and moisture (H₂O). Platinum group metals (PGMs) are present in very small quantities in these class of catalysts and, given their intrinsic value, it is worth recovering them from the spent exhaust systems [2,3]. However, for such PGM recovery processes to be cost-effective, well over 90% of these precious metals must be recovered [3].

This paper is concerned with an assessment of the recovery mechanism of PGM in one family of pyrometallurgical processes that treat the catalysts from the spent exhaust systems. A brief survey of these processes is followed by a straightforward analysis of the presumed mode of operation. Simply put, the available experimental data does not support the conventional received wisdom on the way in which the PGMs are recovered. The paper then suggests a possible mechanism by which the PGM is recovered in the collector metal.

2. Automotive catalytic converters and the PGM recovery issue

Since the mid-1970s, the demand for PGM use in automotive catalytic converters has become the dominant market for platinum and rhodium. By 1996, the annual demand for PGM use in this sector was well over 120 000 kg (52 000 kg for platinum, 65 000 kg of palladium and 1000 kg of rhodium) [2].

Scrap catalysts from automotive vehicles contain an average of one kilogram of PGM per tonne of catalyst, with a 1995 value of US\$15 000 [3]. US legislation (and elsewhere) requires the removal of catalysts prior to the dismantling and crushing of scrap automotive vehicles. The potential financial rewards of PGM recovery from automotive catalyst converters points the way to an environmentally friendly profitable business, for companies with an efficient process. Moreover, in the 20 years since 1975, although more than 568 000 kg of PGMs have been used in automotive catalysts in the USA alone, only 56 800 kg have been recovered [3].

There are a range of hydrometallurgical or pyrometallurgical processes used in PGM recovery [3]. Pyrometallurgical processes have the potential for high recovery rates as well as coping with the impurities found in catalysts [4–7].

In this study, we have focused upon a well-documented recovery process developed at Johnson–Matthey, known hereafter as the JM process [5–7]. This process involves the melting of crushed ‘autocat’ (i.e. catalytic material taken from automotive exhausts and then crushed) and flux materials in a crucible containing a molten collector metal such as iron or copper, using a plasma torch. The resulting molten slag is allowed to settle for a period of time while the PGM is recovered into the collector metal at the base of the crucible (see Fig. 1). Operating temperatures are in the range 1500–1650°C. The collector metal is then tapped off and the PGM

recovered from this by conventional refining techniques. In commercial operations, overall PGM recovery rates of $\sim 95\%$ are achieved from a charge with very low concentrations of PGM ($< 0.1\%$). However, given the financial premium on any improvements in the recovery, there is a motivation to optimise the process if at all possible.

3. Analysis of the JM process

3.1. The key issue

There is one key issue in improving both PGM recovery level and rates in the JM process (and similar pyrometallurgical processes): the settling behaviour of the PGM and its recovery in the collector metal. The operating temperature of the furnace is $1500\text{--}1700^\circ\text{C}$, below the melting point of the PGM material. Hence, it must be assumed that the PGM is present in the autocat slag in the form of small particulates. As such, it is the forces that act on these particulates and their transport behaviour in the bulk slag that controls the settling time. The filling and melting phase involves a stirring of the bath, which is followed by a relatively quiescent phase whereby the PGM settles out into the collector metal (either copper or iron).

Certainly, the patents describing the JM process and related material assume that the PGM particulates have a large enough diameter that they will essentially settle under gravity. Furthermore, the operational perspective clearly assumes this to be the process behaviour.

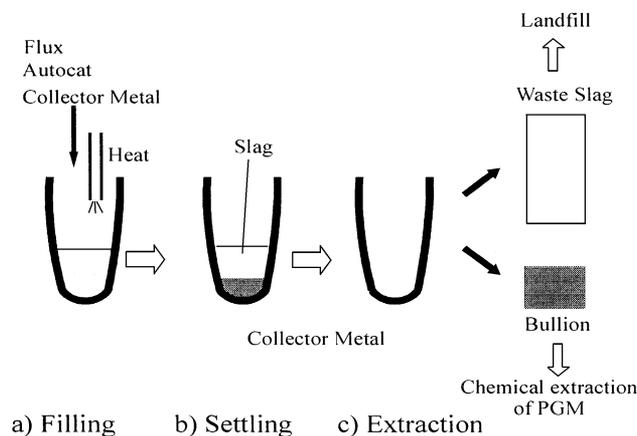


Fig. 1. Schematic outline of the JM process.

3.2. Straightforward approach to analysis

The authors analysed the existing process in order to try and identify ways of optimising its operation. Given the assumed predominant settling mechanism, some simple calculations were carried out to calculate settling times, in the metal–slag complex. Assuming the PGM particles move through the liquid independently (i.e. they do not interact), which is a reasonable assumption since PGM is more dense than both the slag and collector metal, and is < 0.1% by mass of the slag matrix, then Stokes law should give a reasonable estimate of the residence time. Stokes law [8] gives the velocity that balances drag against buoyancy forces, i.e.

$$u_T = \frac{(\rho_p - \rho_L)d_p^2 g}{18\mu} \quad (1)$$

where u_T is the terminal velocity of the settling particle, ρ_p is the particle density, ρ_L is the fluid (liquid slag matrix) density, d_p is the particle diameter, μ is the slag viscosity and g is gravity.

The average settling time, t_s is simply given by

$$t_s = \frac{H}{2u_T} \quad (2)$$

where H is the height of the bath above the collector metal zone. This equation simply assumes that the PGM is uniformly mixed in the slag bath when the settling begins. Of course, it will not be precise because there will be residual stirring at the end of the charging/melting phase, but Eq. (2) should provide a reasonable estimate of the settling time.

3.3. Evaluation of experimental data using Stokes law

The JM patent records a range of experimental data to demonstrate that their process works. The following analysis uses the data on Case 8 [6] because it was perceived as fairly typical. The crushed autocat comprised the following: cordierite substrate, 10 wt.% lime (as the fluxing agent), and 5 wt.% iron filings (as the collector metal). The composition of the slag is 35.5 wt.% Al_2O_3 , 42.9 wt.% SiO_2 , 9.8 wt.% MgO and 7.9 wt.% CaO . It was assumed that the concentrations of PGM and iron filings are too low to affect the slag properties during the settling phase. The settling phase for this case is 10 min at 1560°C.

In this analysis, the PGM particles are assumed to have the properties of platinum (since it is the most common PGM present) with a density of 19 000 kg/m^3 , and to move at the terminal velocity as calculated by Stokes law. The viscosity of the slag is calculated as 3.12 Pa from the Frenkel equation [9], and its density is calculated using the Mills and Keene relation [10]; for this case, the slag density is 2691 kg/m^3 .

Using these data in Eqs. (1) and (2) for a 70 mm slag height, Fig. 2 shows the PGM particle residence time as a function of PGM particle diameter. In the experiments described by Burnham et al. [6] in the JM patent, the settling period is

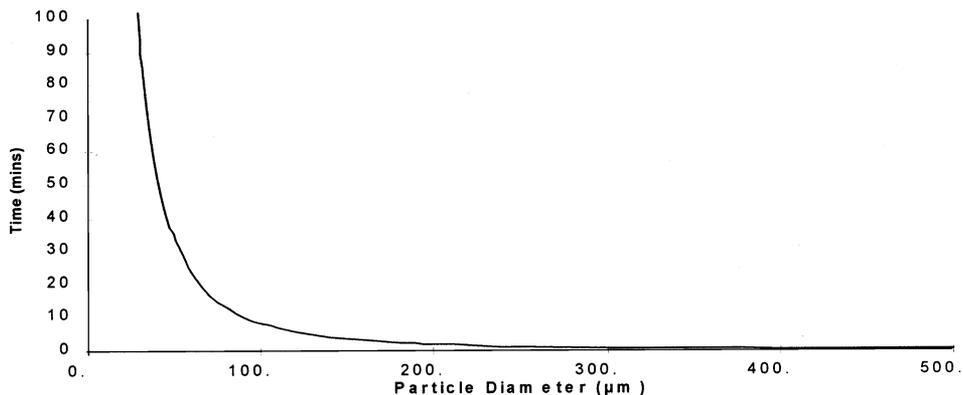


Fig. 2. Variation of residence time with platinum particle size using simple Stokes law.

10 min. This would imply that the PGM particles have a diameter of 200 μm . However, it is clear that PGM particles cannot be readily observed in the slag: Mishra and Reddy [4] suggest that PGM particles are much smaller, of the order of 1–20 nm. Hence, to achieve a diameter of 200 μm , the PGM particles must sinter into agglomerates within the furnace. This seems rather unlikely, as such cluster sizes would be relatively very large and difficult to sustain!

3.4. Discussion of analysis

The presented analysis leads to two incompatible conclusions.

1. For PGM particles to settle by gravity in the experimentally observed timescale, they need to be of the order of 200 μm .
2. PGM particles cannot easily be observed directly in the autocat, and the best estimates of their size is 1–20 μm .

This must mean that the recovery process cannot be driven from the fall of PGM droplets by gravity. Another key process must be occurring to enable the PGM recovery, which has not been expressed in the public domain.

Obviously, the collector metal plays an important role in controlling the efficiency of the process. It seems likely that the slag and collector metal (iron or copper) particles are well mixed by the effects of the plasma torch; as the collector metal is melted into droplets [7], it becomes distributed throughout the slag. It appears that the PGM particles have a strong affinity for the metal droplets [7]. This causes the PGM particles to be attracted and then attached to the metal droplets. Essentially, the more intense the mixing, the more likely the PGM particles are to attach to the metal droplets. It is after the plasma torch is turned off that the metal droplets then fall to the bottom of the vessel due to gravitational forces. Hence, the proposed mechanism of PGM recovery is illustrated in Fig. 3 and is a multiphase process:

- the crushed autocat and collector metal particles are both mixed in a vessel, and melted by the action of the plasma torch;
- as the metal becomes liquid, as droplets, and mixes with the now liquid slag, the PGM particles are swept by the relatively large droplets and become attached to (more likely, absorbed by) them;
- when the plasma torch is turned off, the metal droplets (containing the PGM material) will settle and collect at the bottom of the vessel.

This explanation is at least consistent with the experimental evidence, i.e. the collector metal is mixed with the autocat feed, which has the effect of maximising the potential contact of PGM with metal droplets during the intensive mixing phase.

If this mechanism is indeed correct, then there will be a number of factors that will affect the PGM recovery rate:

- the rate at which the collector metal droplets settle;
- the collector metal droplet size distribution;
- the period of time the collector particles/droplets must be intensively mixed within the bulk slag.

The experimental data in the literature is sparse and does not address the process analysis issues in any kind of structured way. Hence, while the above mechanism may be correct, it has yet to be established and the process evaluated from this perspective.

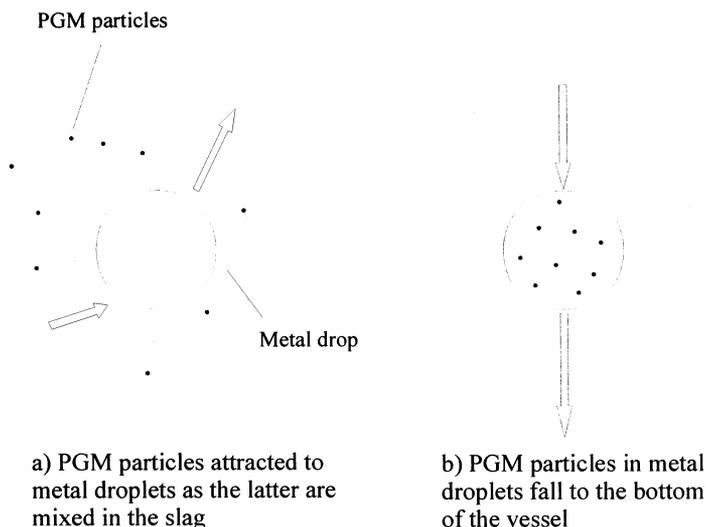


Fig. 3. Proposed mechanism for the collection and recovery of PGM material from the JM process.

4. Conclusions

From an assessment of the JM process for PGM recovery from spent automotive catalytic converters, it is clear that the perceived mechanism by which the PGMs are recovered is flawed. However, the suggested process route appears to be consistent with the data available and could, ultimately, provide the basis from which the process can be optimised.

In the next stage of this work, two mutually interacting themes will be pursued:

- the development of a more comprehensive mathematical model as the basis for a more rational process analysis;
- the design and performance of a series of well-controlled experiments to assess the impact on the recovery efficiency of varying the key set of process parameters.

The combination of the models and experiments, designed to confirm the presented proposition, should then provide a rational basis for optimising the process. Progress on these stages of the work will be reported in due course.

References

- [1] Hennion FJ. Availability of precious metals from spent catalysts. Platinum group metals — an in-depth view of the industry. 1983 IPMI Seminar, Williamsburg, VA, 10–13 April 1983. pp. 61–81.
- [2] Platinum 1997. Johnson Matthey plc, London, 1997.
- [3] Kuczynski RJ, Atkinson GB, Dolinar WJ. Recovery of platinum group metals from automobile catalysts — pilot plant operation. In: Queneau PB, Preston RD, editors. Third International Symposium on Recycling of Metals and Engineered Materials. The Minerals, Metals & Materials Society, Warrendale, Pennsylvania, 1995. pp. 527–541.
- [4] Mishra RK, Reddy RG. Pyrometallurgical processing and recovery of precious metals from autocatalysts using plasma arc smelting. Proceedings of International Precious Metals Institute, Pensacola, Florida, 1986. pp. 217–230.
- [5] Gibbon A, Harry JE, Hodge D. The plasma process for the recovery of the platinum metals from autocatalysts. Proceedings of International Symposium on Plasma Chemistry-8, Tokyo. Paper number D11-03, 1987.
- [6] Burnham RF, Harry JE, Gibbon A. Plasma arc furnaces. European Patent Application 0096 493 A2, 1983.
- [7] Saville J. US Patent 4 685 963, 1987.
- [8] Szekeley J. Fluid Flow Phenomena in Metals Processing. New York: Academic Press, 1979.
- [9] Urbain G. Viscosity estimation of slags. Steel Research 1987;58(3):111–6.
- [10] Mills K.C.B., Keene B.J., Physical properties of BOS slags. International Materials Review 1987;32(1–2):1–120.