Catalytic Filters Control Diesel Engine Exhaust

PARTICULATE EMISSIONS SUBSTANTIALLY REDUCED USING PLATINUM GROUP METAL CATALYSTS

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Diesel-engined vehicles are highly reliable and use fuel more economically than spark ignition engines, therefore they are being more widely adopted. However, in addition to relatively small quantities of gaseous pollutants, diesel exhaust emissions characteristically contain much higher concentrations of particulate materials. Continuing their clean air policy, the Environmental Protection Agency in the United States of America has imposed limits on the amount of particulates that will be tolerated in diesel exhaust emissions from 1982 model year vehicles to 0.6 grams per mile, with an even lower limit of 0.2 grams per mile proposed for the 1985 model year. The generation of particulates is complex and involves many parameters; this paper discusses the development of an after-treatment system employing platinum group metals that has now successfully controlled particulate emissions during a 50,000 mile durability trial.

The use of catalysts to control the gaseous emissions from gasoline-fuelled spark ignition engines is now well established in the United States and Japan, where platinum metal catalyst systems have proved to be effective for lowering such exhaust emissions to levels that satisfy the stringent requirements of the Environmental Protection Agency (E.P.A.) and the Japanese Government, respectively.

The concentrations of carbon monoxide and hydrocarbons present as gaseous emissions in the exhaust from a diesel engine are substantially less than in that produced by a spark ignition engine. However, diesel exhaust is characterised by smoke or particulate emissions. Since these particulates are solid phase species the techniques required to control them are very different from those used successfully for gaseous emissions.

Particulates are defined as solids that can be collected at a temperature of 55°C, this being an E.P.A. test temperature. They contain solid carbon and many condensed high molecular weight hydrocarbons, together with adsorbed gaseous species. Being visible, such emissions have long been regarded as a nuisance but recently it has been recognised that some of the hydrocarbon components are carcinogenic and that diesel particulates are mutagenic. These particulates may be removed from the gas stream by filtration. Many forms of filter would do this but their application in automobiles is limited by considerations such as size, weight or feasibility. Filtration is purely a mechanical process so the material filtered out has to be disposed of in a non-polluting manner, and this presents a problem. The filtered, or trapped, particulate may be conveniently destroyed by burning, which can be done at temperatures of 600°C, or above. However, diesel engines

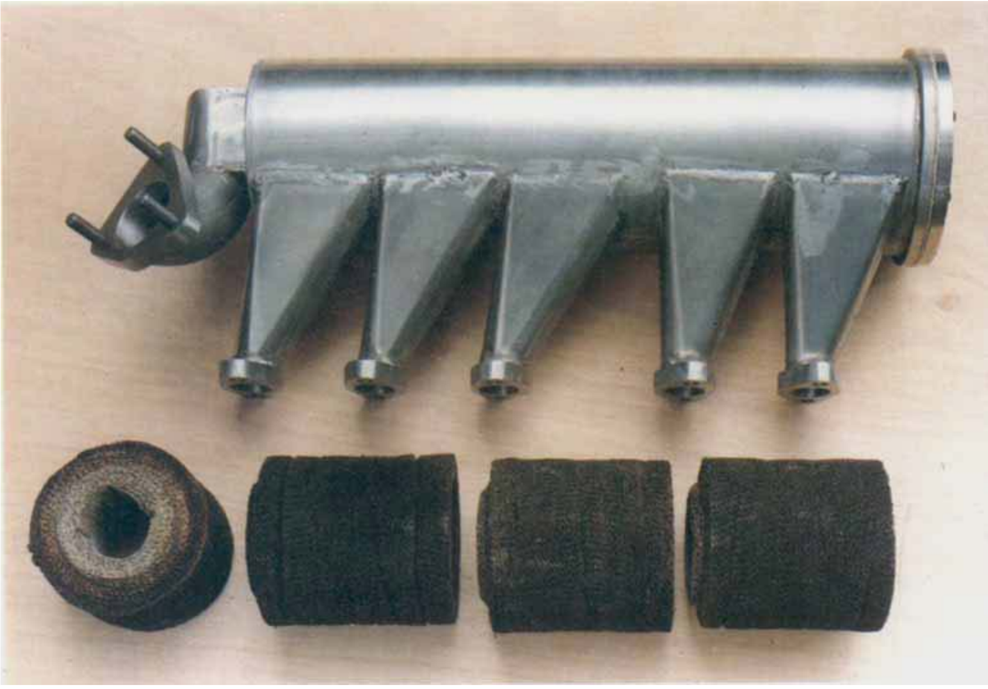

Fig. 1 During early work catalytic filters in the form of radial flow annuli were mounted in an exhaust manifold. To make best use of the exhaust temperatures, this was mounted as close to the engine as possible, replacing the original exhaust manifold

characteristically have an exhaust temperature much below this. When a vehicle is in road service, typical exhaust temperatures will be in the range 100 to 350°C. Early work established that platinum metal catalysts were capable of initiating this burn-off process at temperatures well below 600°C, and this article considers such catalytic filters.

Filtration

Filtration can be carried out by two basic routes: (a) filtration through a medium having a smaller pore size than the material to be filtered out, and (b) filtration by impingement, the impact resulting from changes in the direction of the passages through the filter material and the momentum of the solid particulates to be filtered out.

Many forms of impact filtration unit were examined including axial flow, radial flow, and granular or pellet filters. It was found that a radial flow system gave the greatest flexibility

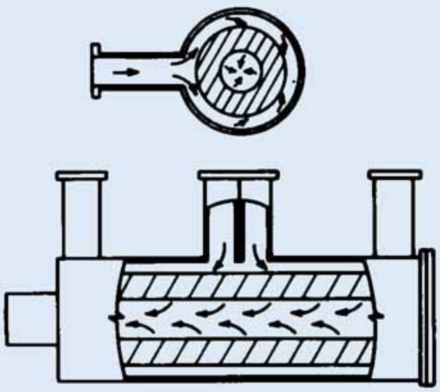

Fig. 2 This is a schematic representation of a catalytic manifold. Each exhaust port has a runner designed to cause the exhaust gases to enter the body of the manifold circumferentially, resulting in an even distribution of the gases around the outside of the filter annuli

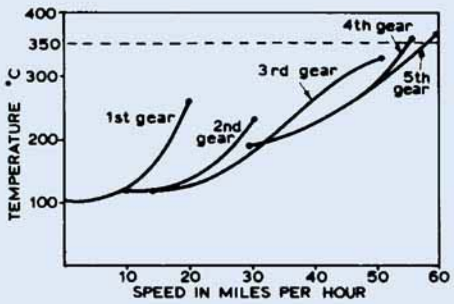

Fig. 3 Test data collected from a typical 2 litre naturally aspirated diesel engine shows that for a large part of the time that the vehicle is running the exhaust temperature is below that necessary for the catalyst to light off

without undue back pressure, and enabled many filter materials to be tested. The filter units consist basically of a mesh of stainless steel wires formed into radial flow annuli through which the exhaust gases can pass. The steel wire substrate is covered with a thin alumina washcoat which supports the platinum group metals catalyst, and must combine maximum surface area with minimum obstruction to flow.

While platinum was initially used as the catalyst, specially promoted platinum formulations have now been developed for this particular application in order to minimise the production of unwanted sulphate emissions.

During early work the filtration performance of several different types of unit was evaluated on a European, 2 litre, naturally aspirated diesel-engined passenger car. For this, radial filters were mounted into an exhaust manifold as illustrated in Figure 1, and also shown schematically in Figure 2.

Practical Vehicle Installation

Major parameters affecting the design of a catalytic filter system for diesel engine emissions control are engine displacement, engine type and exhaust temperature. Due to their unthrottled breathing characteristics, larger airflows are encountered with diesel engines as compared with gasoline engines of the same displacement. Thus the overall size of a catalyst necessary for a diesel engine is generally larger than that for a comparable gasoline engine.

The platinum metals catalyst formulation now developed for this diesel application requires a temperature of approximately 350°C for the oxidation of particulates from naturally aspirated engines. However, temperatures of this magnitude are generally encountered only during the high load conditions that form just a part of the normal operating range of a typical automotive diesel engine. Road load temperature versus speed data for a typical 2 litre naturally aspirated diesel engine with a five speed, standard transmission is given in Figure 3. The temperature measurements were made in the exhaust pipe approximately two feet from the outlet of the exhaust manifold. The data shows that for a large part of the time that the vehicle is running the exhaust temperature is below 350°C, the temperature required for the catalyst to promote the oxidation of the particulates. Clearly the catalytic filter must have the ability to store the particulates collected during the time that the exhaust gas temperature is below that required for instantaneous oxidation, and to be able to do this for an acceptable period of low speed driving. Cleaning of the filter will normally occur when a change in engine operating conditions causes the exhaust temperature to rise above 350°C, that is above the catalyst light-off temperature; but in case this does not happen before the efficiency of the catalytic filter is impaired components are now included in the system to activate regeneration when a pre-set back pressure is reached.

All preliminary work on diesel exhaust emissions control involved manifold mounted catalysts. To make best use of the available exhaust temperatures from the naturally aspirated engines, these were mounted as close to the engine as possible where they replaced the original exhaust manifold, and in addition they were insulated to conserve exhaust heat. The final system developed in Stage I of the

Table I

12,500 Mile Durability Test on a JM4 Manifold Unit, LA–4 (hot start) Cycle of the Federal Test Procedure (Emissions in grams per mile)

Mileage	Condition	HC	CO	NO_x	Particulate	Sulphate
0	Baseline	0.418	1.32	1.58	0.572	0.0080
0	Catalyst	0.090	0.167	1.46	0.025	0.0067
600	,,	—	—	—	0.215	0.0075
1200	,,	—	—	—	0.238	0.0073
1800	,,	0.160	0.229	1.61	0.205	0.0094
3000	,,	0.126	0.400	2.04	0.311	0.0350
3600	,,	0.167	0.323	1.92	0.304	0.0408
4200	,,	0.125	0.348	1.92	0.283	0.0229
4900	,,	0.090	0.324	1.64	0.263	0.0146
5500	,,	0.117	0.260	1.63	0.227	0.0191
6000	Baseline	0.389	1.504	1.75	0.528	0.0153
6100	Catalyst	0.130	0.326	1.74	0.292	0.0410
8500	,,	0.136	0.157	1.73	0.301	0.0280
12,500	Baseline	0.419	1.152	1.93	0.541	0.0113
12,500	Catalyst	0.122	0.340	1.68	0.288	0.0123

Table II

50,000 Mile Durability Test on a JM13 Underfloor Mounted Unit, Federal Test Procedure (Emissions in grams per mile)

Mileage	Condition	HC	CO	NO_x	Particulate	Sulphate
0	Baseline	0.24	1.01	0.90	0.225	0.00360
0	Catalyst	0.05	0.16	0.79	0.113	0.00175
5000	Baseline	0.19	0.82	0.89	0.259	0.00554
5000	Catalyst	0.05	0.18	0.89	0.135	0.00734
10,000	Baseline	0.19	0.84	0.90	0.211	0.01370
10,000	Catalyst	0.06	0.24	0.94	0.129	0.01102
15,000	Baseline	0.23	0.92	0.81	0.227	0.01100
15,000	Catalyst	0.10	0.31	0.79	0.111	0.00945
20,000	Baseline	0.19	0.79	1.00	0.275	0.01240
20,000	Catalyst	0.05	0.27	0.87	0.111	0.00475
40,000	Baseline	0.17	0.85	0.85	0.213	0.00208
40,000	Catalyst	0.10	0.49	0.92	0.099	0.00167
50,000	Baseline	0.22	0.92	1.04	0.277	0.00928
50,000	Catalyst	0.10	0.55	0.86	0.167	0.00452

initial research project, and known as JM4, gave filtration to 0.2 grams of particulate per mile on a 5 cylinder, 2 litre, 4 speed European vehicle, having baseline of 0.54 grams per mile. The data from a 12,500 mile durability run are presented in Table I and indicate the successful completion of Stage I of the project, that is the development of a research concept diesel emission control package.

Stage II of the research project commenced

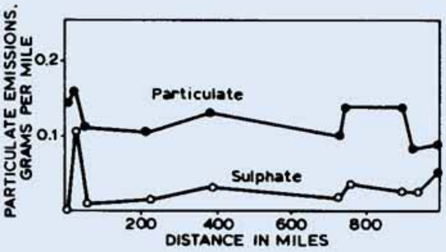

Fig. 4 Data from a JM13 manifold unit during the hot start LA-4 cycle shows particulate emissions to be substantially below the LA-4 baseline particulate level of 0.48 grams per mile. Although some increase in sulphate emissions occurred, the amount was not significant

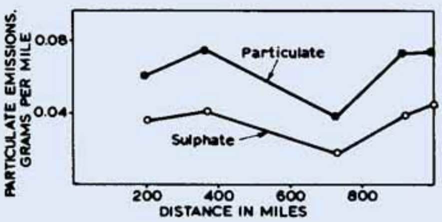

Fig. 5 Data collected during testing of a JM13 manifold unit over the Federal high speed test procedure shows that the higher running temperature reduces the amount of particulate emissions to a very low level, compared with the HFET baseline of 0.25 grams per mile. While sulphate emissions are above the 0.014 grams per mile baseline they still represent only a very small conversion of the total sulphur to sulphate

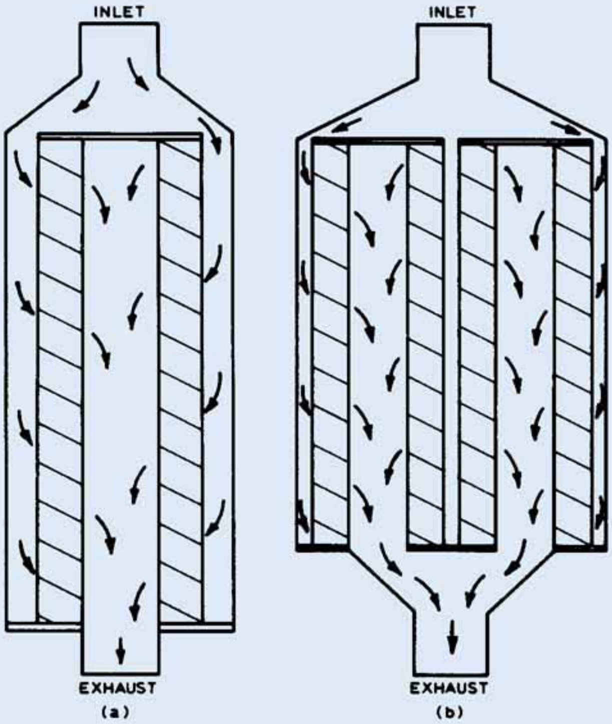

Fig. 6 Underfloor mounted units resemble a conventional silencer in shape. The exhaust gases flow round the perimeter of the can then flow radially into the hollow central core. Single column (a), and multiple column (b) units have been designed

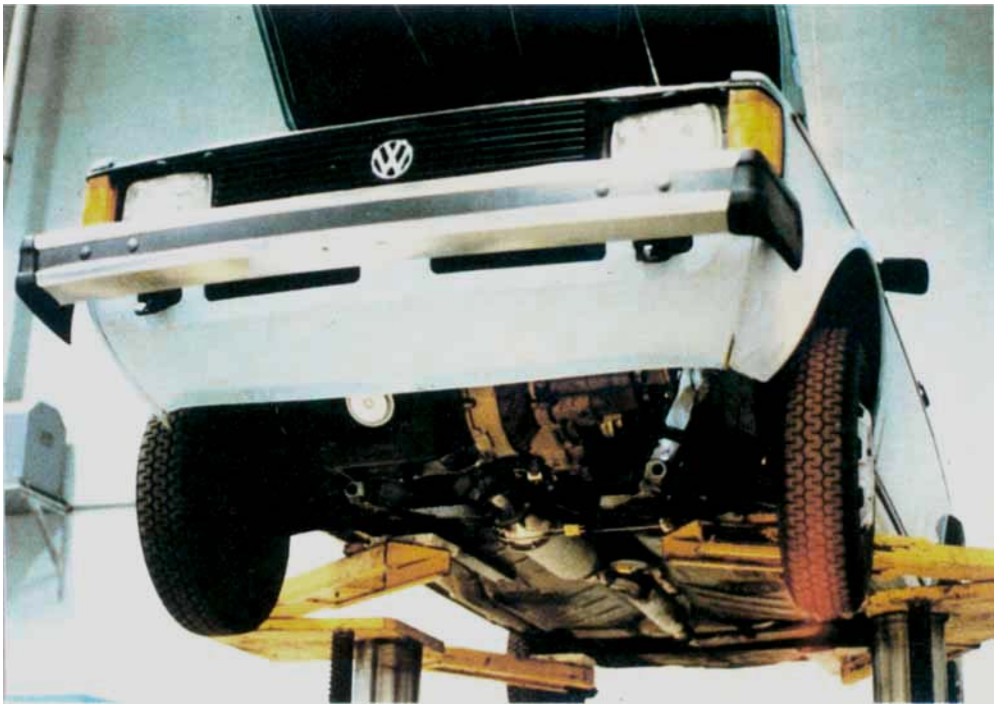

Fig. 7 A JM13 underfloor catalytic filter is fitted in a similar position to the catalyst on the gasoline-fuelled version of the Volkswagen Rabbit

with the development of an improved filtration system. Various units were tested, mainly in manifold reactors, leading eventually to the development of JM13, which incorporates the specially formulated promoted platinum catalyst. Figure 4 summarises particulate and sulphate emissions data obtained with a JM13 unit mounted on a European vehicle with a 5 speed manual transmission and a 2 litre, 4 stroke naturally aspirated engine, tested to 1,000 miles over the hot start LA-4 cycle of the Federal Test Procedure. The same emissions measured over the Federal high speed test (Highway cycle), where higher catalyst temperatures result in less pollutants are presented in Figure 5.

The second phase of the project involved the extension of the research concept into the development of a system that it would be feasible to produce. Since both transverse mounted engines in front wheel drive compact cars, and turbocharged engines, pose space problems for the installation of a manifold system, an underfloor mounted system downstream from the engine was a prime requirement. Cost considerations and the interchangeability of filter units added to the problems for such underfloor mounting locations. As established earlier, the temperature drop in the exhaust system must be minimised to aid catalyst performance. In order to reduce the heat losses that would occur with underfloor mounting the catalyst is positioned as close to the engine as possible. In addition the catalyst and the exhaust system up to and including the manifold are insulated. An advantage of underfloor mounting is the ability to use parallel runs of radial flow filters, if necessary, for large engines. An underfloor reactor resembles a conventional silencer in shape. The unit is baffled to allow the exhaust gas to flow round the perimeter of the can, enter the catalytic filter and flow radially into the hollow central core before passing out of the exit. Units have been designed with one single central column of catalyst or with multiple parallel columns, as space permits. A typical 2 litre unit and a larger unit for a 5.7 litre V8 diesel are shown schematically in Figures 6(a) and 6(b). Such underfloor units are simpler to design, produce and fit to a vehicle, and are easily adapted to turbocharged engines compared to the manifold type of catalytic filter. On many vehicles, the units fit into the space normally occupied by the catalyst on vehicle models fitted with gasoline engines.

System Durability Determination

With the development of the catalytic filter and the related support systems showing successful control of diesel exhaust emissions on short term testing, an independent durability evaluation to 50,000 miles was commissioned at Southwest Research Institute in San Antonio, Texas. A Volkswagen Rabbit (Golf) was selected as the test vehicle, being a typical example of a diesel powered automobile of the mid 1980s. The vehicle was a 1981 model fitted with a 1.6 litre, 4 cylinder indirect injection engine, and having 4 speed manual transmission. The car purchased was tested as delivered, the only changes being the addition of a JM13 underfloor catalytic filter and related system components, Figure 7.

The engineering target for the efficiency of the catalytic filter was a 50 per cent reduction in baseline particulate emissions, to give between 0.1 and 0.15 grams per mile. The filter, 14 inches long and 5.5 inches in diameter, was mounted in the exhaust train adjacent to the

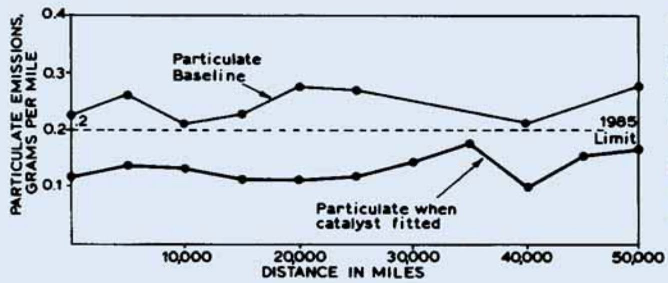

Fig. 8 This plot of particulate emissions against distance covered, during the evaluation to 50,000 miles of a JM13 unit, shows the emissions to be within the 0.2 grams per mile proposed for 1985 model vehicles

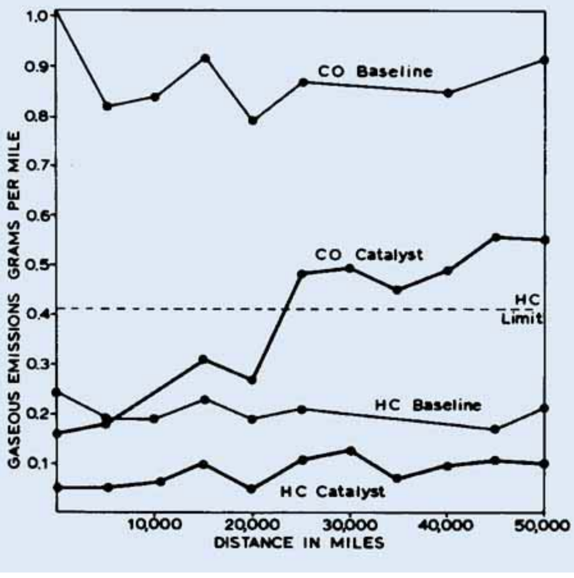

Fig. 9 Throughout the 50,000 miles of the Federal Test Procedure the JM13 catalytic filter gave a significant reduction in gaseous hydrocarbons and carbon monoxide emissions

gear shift linkage in the existing floor hump.

The vehicle was successfully operated over the 50,000 mile test and the particulate emissions were within the 0.2 grams per mile regulations, as determined by the Federal Test Procedure. A selection of the results obtained is given in Table II, and Figures 8 and 9. It will be observed that in addition to the marked reduction in particulate emission there was also a significant reduction in gaseous hydrocarbons, carbon monoxide and odour emissions throughout the test.

Work is now continuing to improve still further these catalytic filter systems.

The work described in this article formed the subject of a SAE Technical Paper, No. 820184, at the recent International Congress and Exposition of the Society of Automotive Engineers, Detroit, Michigan, February 22–26, 1982. The paper "Catalytic Control of Diesel Particulate" presented there by Bernard E. Enga, Miles F. Buchman and Ivan C. Lichtenstein was supported by references and contains much detailed test data.

A Definitive Work on the Mineralogy of the Platinum Group Elements

Platinum-Group Elements: Mineralogy, Geology, Recovery, CIM Special Volume 23, EDITED BY L. J. CABRI, The Canadian Institute of Mining and Metallurgy, Montreal, 270 pages, $40

A considerable amount of new information on the geochemistry and mineralogy of the platinum group elements has been presented in numerous articles published over the last ten to fifteen years. Now the first comprehensive reference source has been produced, based on data compiled up to 1981.

The essential aspects of thermodynamics and inorganic chemistry, and their relevance to an understanding of the geochemistry of the platinum group elements is given. A collection of information on the phase relationships of the platinum metals with those elements which are considered to be mineralogically significant, and their importance in acting as geochemical collectors are exemplified and discussed. Dr. Cabri has carried out an exacting task in identifying, characterising and collating nearly one hundred minerals, and he includes a critical assessment of the base metal minerals which are reported to contain minor quantities of platinum group elements. Of equal relevance to the platinum producers are the chapters devoted to sample preparation and analytical techniques.

The relative importance of the different types of ore, with respect to platinum group element production and resources, are discussed in some detail. The largest and most important deposits occur in the Bushveld Complex of Southern Africa. These consist of the Merensky Reef, the UG2 chromitite layer and the Platreef, which together are estimated to contain total platinum group element resources of some 60×10^6 kg—sufficient to satisfy foreseeable needs for many years to come. Most of the current production comes from the Merensky Reef, where the platinum group metals are the major product. Despite the large variation in the mineralogy of the Reef the platinum : palladium ratio is consistent at 2.5, while mine head grades for total platinum group elements are 6 to 8 grams per tonne. The other major deposits are the Noril'sk-Talnakh combine in Siberia, U.S.S.R., and the Sudbury district of Canada. In both cases the platinum group elements are by-products from the copper-nickel sulphide mines and have much lower platinum : palladium ratios; at Noril'sk it is 0.4. Most of the information on the recovery of the platinum metals is concerned with beneficiation techniques and their relationship to the mineralogy of different ores.

Inevitably in a book of this nature there is some duplication of material, however the index is sufficiently detailed to enable readers with differing interests to locate appropriate information. References are given at the end of each chapter.

In addition to providing an excellent and much needed compilation of data on the geochemistry and mineralogy of the platinum group elements, which will be a definitive work for years to come, the volume also demonstrates that there is still considerable debate on the genetic relationships of the platinum group elements, and it helps to define areas for future research. J.G.D.