Challenges in crucible- and pilot-scale refining of a PGM-bearing iron alloy

Mr Moholwa S.M.[1], Mr Tsebe S.P.[1], Dr Matinde E[1,2].
[1]Mintek, [2]Wits University

Presenter:
Mr Sam Moholwa, Mintek

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Presentation overview

- Introduction
- Test work objectives
- Experimental methods
- Results and discussions
- Conclusions
- Recommendations

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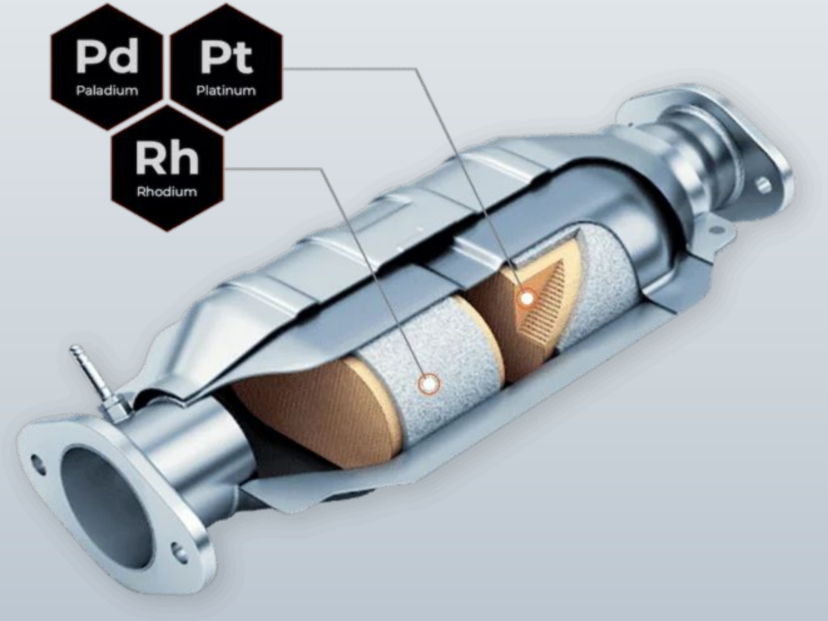
Introduction

- PGMs are scarce and expensive
- Used in the petrochemical and automobile industry
- 42% Pt and 82% Pd of total global demand used in the automobile industry[1]
- PGMs uneven distribution necessitate recycling
- Secondary resources contains higher PGMs compared to primary resources



Source:[2]

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1. Alison, C., 2024. PGM market report. Johnson Matthey.URL: https://matthey.com/documents/161599/509428/PGM-Market-Report-24.pdf/4d557d3b-47d1-d975-c4af-5df1c81000f0?t=1715228936090
2. https://elvatech.com/sample-preparation-of-autocatalysts-for-xrf-analysis/ (accessed 21 October 2025)

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Test work objectives

- Project objectives
  - *To evaluate technical feasibility of upgrading the PGMs' content of the alloy from 3% to 20% through oxygen refining*
  - *To gain insights into crucible behaviour, slag chemistry and oxidation control*

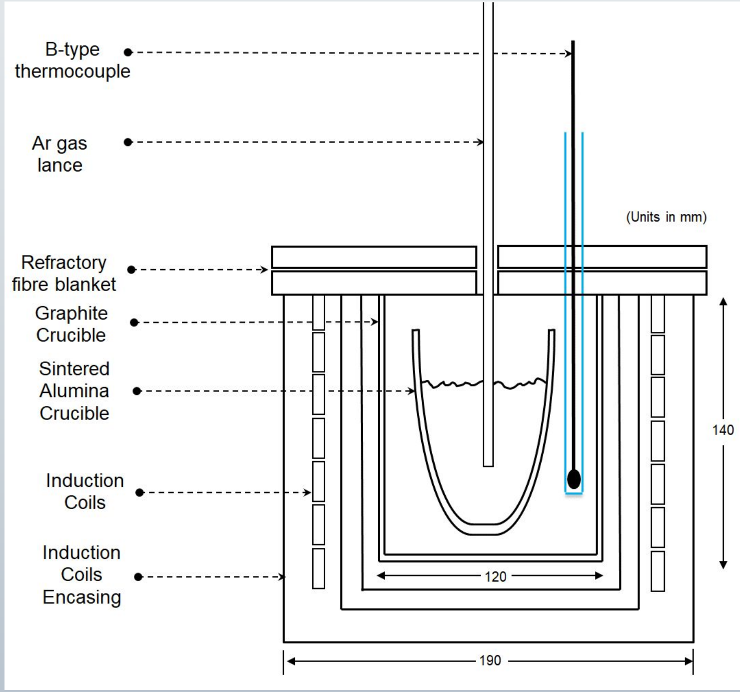
- Test work stages
  - *Stage 1 – Exploratory tests (in an induction furnace)*
  - *Stage 2 – Optimization tests (in an induction furnace)*
  - *Stage 3 – Pilot scale tests (in a TBRC)*

Experimental methods

- Raw materials
  - *PGMs-containing Fe alloy*
  - *Silica powder ~98%SiO_2 - chemical grade*
  - *Lime powder ~98% CaO - chemical grade*
  - *Alumina powder ~ 98% Al_2O_3 - chemical grade*

Fe	Pd	Pt	Rh	Cu	Ni	PGMs	Total
90.2	1.97	1.23	0.22	5.10	0.64	3.42	99.5

- Tests made use of 100 and 500 ml high quality fused alumina crucibles



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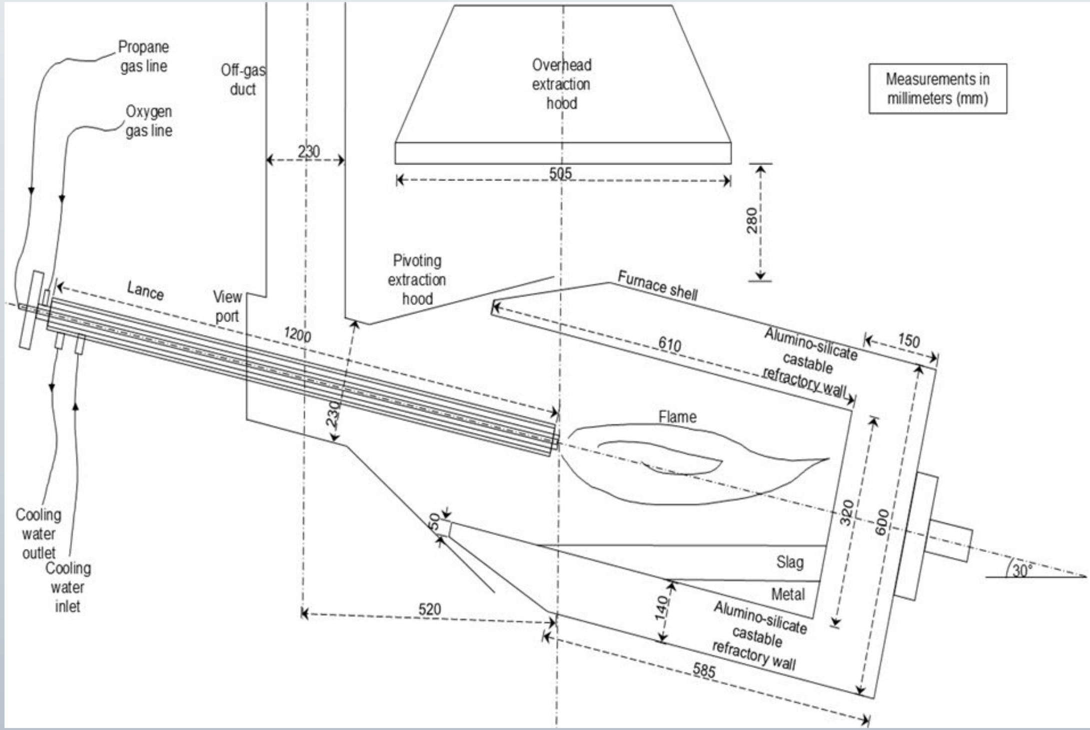
Experimental methods

- TBRC (Used for pilot scale tests)
- Consists of:
  - *Oxy-propane gas burner*
  - *Rotary furnace*
  - *Off-gas handling system*

- Gas supply
  - *Oxygen (O_2) gas, industrial grade at line pressure of 400 kPa(g)*
  - *Propane (C_3H_8) gas, industrial grade at line pressure 100 kPa(g)*



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Experimental methods

- Crucible tests
  - *Pack a pre-determined alloy mass*
  - *Place crucible in the furnace*
  - *Heat up at 10°C/min under Ar gas*
  - *Check temperature of molten alloy*
  - *Inject O_2 gas at 100-500 ml/min into the molten alloy*

- TBRC tests
  - *Warm up furnace to >1000 °C for a period of 2.5h*
  - *Divide pre-determined mass into 4 equal bags*
  - *Feed 1 bag once vessel wall is at 1400°C*
  - *Feed another bag once molten until all 4 are fed*
  - *Switch to oxidising flame to start oxidation at 160 mol% O_2 flame stoichiometry*

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Results and discussion – Stage 1

- To understand alloy behaviour
- Six test conducted in this stage
- Three tests terminated prematurely due to crucible failure
- It was established that the alloy was molten at temperatures above 1470°C

Test	Start alloy mass, g	Temp before Blow, °C	Oxygen delivered, g	Oxygen delivered, %	Final alloy mass, g	Alloy mass loss, %	Al_2O_3 added, g	CaO added, g	SiO_2 added, g
1	102	1510	8.14	7.98	39.6	61.3	-	-	-
2	100	1466	8.14	8.14	-	-	2	2	2.0
3	90.0	1524	5.57	6.19	33.0	63.3	-	-	-
4	182	1503	9.86	5.42	128	29.9	2	-	4.0
5	186	1509	18.7	10.1	98.9	46.9	6	-	18
6	200	1525	9.86	4.93	-	-	4	-	12

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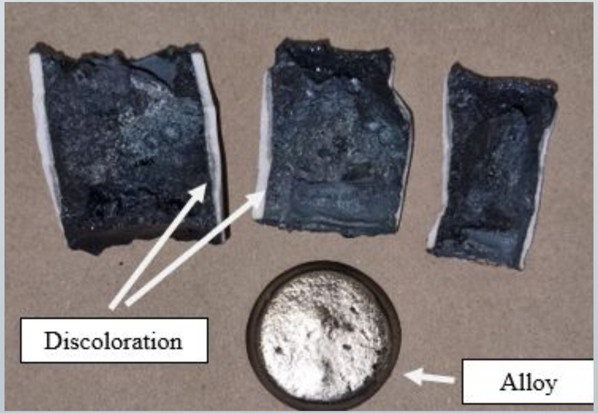
Results and discussion – Stage 1

- Severe chemical erosion of crucible wall led to premature crucible failure
- Test 1, 3 & 6 terminated due to crucible failure
- Termination reason: Test 3 - insufficient metal bath, Test 4 - freezing slag and Test 5 full crucible

Test	Fe	Pd	Pt	Rh	Cu	Ni	PGMs	Total
1	82.0	3.89	2.58	0.51	8.27	1.37	6.98	99.4
3	89.5	2.24	1.32	0.22	4.82	0.55	3.78	99.8
4	89.0	2.35	1.40	0.22	4.91	0.55	3.97	99.5
5	86.2	3.07	1.76	0.32	5.99	0.73	5.15	99.1
6	84.6	3.30	1.85	0.34	6.21	0.78	5.49	98.2



Test	FeO	Al_2O_3	Cr_2O_3	CuO	NiO	SiO_2	Total
1	81.0	14.7	0.89	0.40	0.21	0.91	98.0
3	83.5	8.21	0.91	0.42	0.22	0.86	94.1
4	82.5	10.6	0.91	0.41	0.17	5.60	100
5	77.5	16.9	0.90	0.48	0.23	3.39	99.4

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Results and discussion – Stage 2

- To evaluate deportment of key elements
- Eight tests conducted in this stage
- Six tests terminated prematurely due to crucible failure

Test	Start alloy mass, g	Temp before Blow, °C	Oxygen delivered, g	Oxygen delivered^, %	Final alloy mass, g	Alloy mass loss, %	Al_2O_3 added, g	CaO added, g	SiO_2 added, g
1	1090	1496	23.3	8.30	931.4	-	4.0	-	12
2	970.0	1503	26.4	10.6	862.6	-	34	-	42
3	500.0	1496	38.6	29.9	323.2	-	48	68	68
4	701.0	1480	27.5	15.2	455.1	-	68	72	72
5	701.0	1489	32.2	17.8	574.4	18.1	72	80	80
6	747.0	1478	30.7	16.0	633.7	15.2	56	64	64
7	713.0	1497	25.0	13.6	617.0	-	56	64	64
8	617.0	1509	26.4	16.6	198.1	-	56	64	64

^Amount of oxygen delivered relative to stoichiometric amount of oxygen required to oxidise all the iron in the alloy.

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Results and discussion – Stage 2

- Severe chemical erosion of crucible wall was still an issue at this stage
- Test 1,2,3,4,7 and 8 terminated due to crucible failure
- Test 1 to 5 and Test 8 used fresh alloy
- Test 6 used alloy from Test 1 and 2. Test 7 used alloy from Test 6

Test	Fe	Pd	Pt	Rh	Cu	Ni	PGMs	Total
1	90.5	1.88	1.20	0.22	5.11	0.60	3.30	100
2	90.9	1.78	1.24	0.22	4.88	0.64	3.24	101
3	88.1	2.44	1.47	0.27	6.41	0.81	4.19	100
4	89.4	2.20	1.35	0.25	5.59	0.74	3.80	100
5	89.4	2.13	1.31	0.24	5.50	0.70	3.68	100
6	89.3	2.23	1.37	0.25	5.70	0.88	3.85	101
7	86.4	2.87	1.76	0.32	7.01	1.01	4.95	100
8	87.1	2.70	1.67	0.30	6.73	0.90	4.67	100

Test	FeO	Al_2O_3	Cr_2O_3	CuO	NiO	CaO	SiO_2	Total
3	67.1	8.65	0.31	0.15	0.01	11.8	11.5	99.5
5	63.1	7.44	0.19	0.14	0.03	17.8	10.9	99.6
6	64.2	7.39	0.09	0.33	0.03	16.1	11.7	99.9

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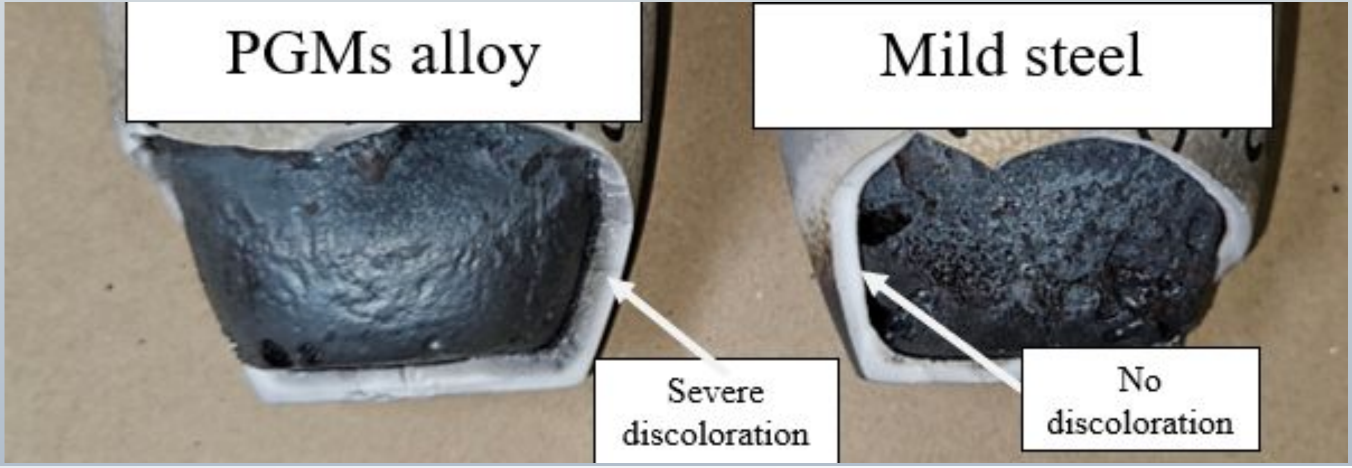
Results and discussion – Crucible failure investigation

- Investigate interaction between alloy and crucible wall
- Re-melting the PGM-bearing alloy and mild steel
- Discoloration observed on the crucible containing PGM-bearing alloy
- SEM analysis revealed inclusions in the walls of crucible containing PGM alloy
- SEM analysis revealed that hercynite layer was formed on the crucible walls of the mild steel test



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Results and discussion – Stage 3 TBRC tests

- All the alloy in Test 1 was oxidised
- The alloy in Test 2 was under oxidised
- The alloy in Test 3 was over oxidised to 58% PGMs
- The alloy in Test 4 was over oxidised to 82%

Test	Start alloy mass, kg	Final alloy mass, kg	Alloy mass loss, %	Al_2O_3 added, kg	CaO added, kg	SiO_2 added, kg	Slag produced, kg	Oxidation duration, Minutes
1	10.0	-	100	1.5	1.5	1.5	18.6	60
2	9.25	6.55	29.1	2.1	2.1	2.1	8.45	110
3	9.25	0.18	98.1	0.8	0.8	0.8	9.16	50
4	7.25	0.30	95.0	0.8	0.8	0.8	8.86	60

Test	Fe	Pd	Pt	Rh	Cu	Ni	Si	PGMs	Total
2	85.2	3.06	2.00	0.37	4.20	0.59	2.33	5.4	97.7
3	22.3	30.1	24.1	3.76	8.10	0.59	9.23	58	98.2
4	1.30	44.0	32.3	5.72	11.1	0.10	3.81	82	98.3

- <u>Key takeaways</u>
  - ❖ *High oxidation efficiency*
  - ❖ *Poor oxidation rate control*
  - ❖ *Poor repeatability*

Test	FeO	Al_2O_3	Cr_2O_3	CuO	NiO	SiO_2	CaO	Total
1	35.2	35.8	0.09	1.60	0.34	6.72	6.42	85.7
2	7.11	47.6	0.11	0.13	0.06	31.7	11.8	98.4
3	21.7	55.9	0.10	0.40	0.31	9.90	11.0	99.3
4	23.9	50.4	0.10	0.50	0.62	12.0	11.0	98.6

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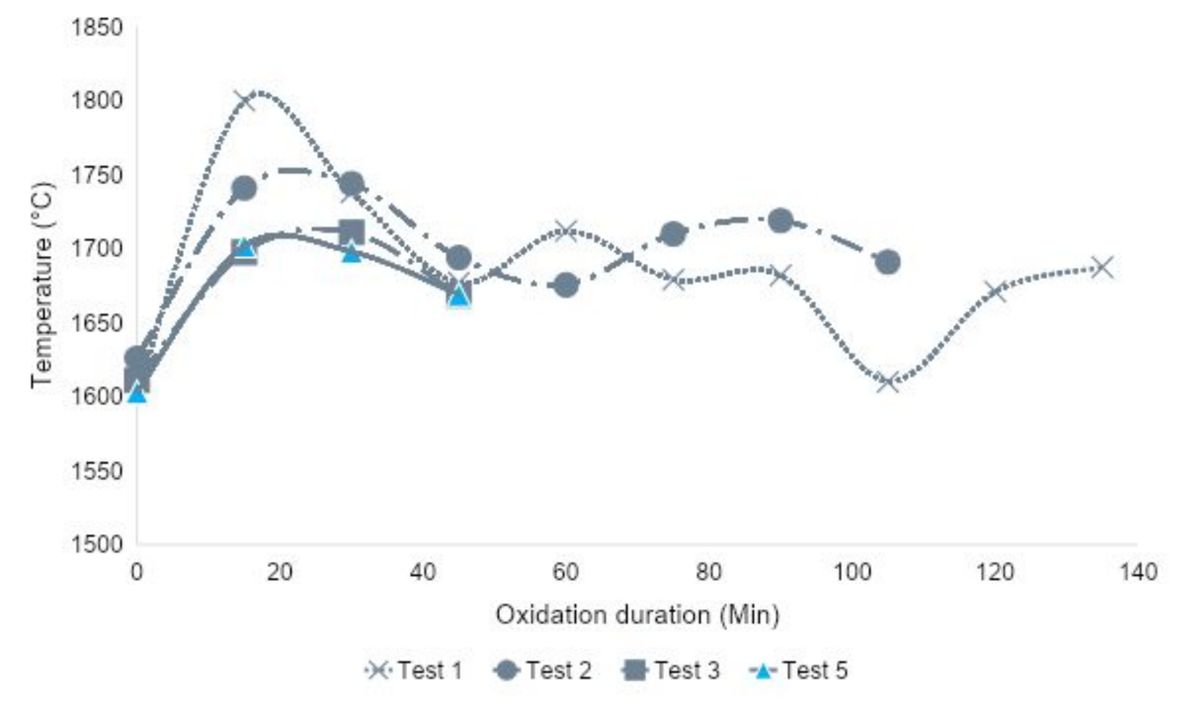
Results and discussion – Stage 3 TBRC tests

- Temperature increased in the first 15 minutes
- Then dropped as oxidation rate decreased



Conclusions

- The crucible scale test work encountered severe premature failures of high-quality alumina crucibles due to chemical attack by both the slag and the alloy.
- This prevented the refining process to progress long enough to demonstrate refining of the alloy to the target PGMs grade.
- Further tests were conducted at pilot scale in a TBRC whereby high oxidation efficiencies were obtained but could not be accurately controlled, leading to over oxidation of the alloy and production of final alloys with PGM grades of more than 80%.
- Therefore, the refining of this particular PGM-bearing alloy was not technically feasible at the crucible scale due to consistent premature failures of the alumina crucibles.
- The refining of the alloy at pilot scale in a TBRC was effective but there was poor control of the oxidation rate and lack of reliable method to measure the oxidation efficiency which resulted in over-oxidised alloys.

Recommendations

Further studies are recommended to evaluate:

- Alternative crucible refractory that can better contain FeO-rich slags
- Better fluxing strategy to dilute the FeO concentration in the slag
- Improved real-time oxidation efficiency measurement method for the TBRC

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200 Malibongwe Drive
Randburg
South Africa

Tel: +27 11 709 4111

www.mintek.co.za

Private Bag X3015
Randburg
2125
South Africa

Mintek MintekSA Mintek_RSA Mintek_RSA