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Development of roasting parameters for the ConRoast process with low-sulphur feedstock

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The ConRoast process for the production of platinum group metals involves the use of a fluidized bed reactor for the removal of sulphur from ore concentrates by roasting prior to smelting in a DC - arc furnace. Test work was carried out in 2007 at Hazen Research in Golden, Colorado to provide the data necessary for a commercial roaster to be designed by Technip. This paper discusses the rationale behind the test work, the goals for calcine composition to be used as smelting furnace feed, the results of various roaster operating parameters in terms of calcine composition (particularly residual sulphur and the fate of trace elements), and the impact of the results in terms of a commercial roaster design.

Introduction

In 2007, Technip was engaged by Mintek to investigate the roasting parameters involved in the removal of sulphur from low-sulphur platinum group metal (PGM) concentrates as part of the ConRoast process.^{1,2} This process involves DC-arc-furnace smelting of dead-roasted PGM ore concentrates, and provides an alternative to traditional matte smelting. One proposed advantage of the ConRoast process over traditional matte smelting techniques is the ability to remove sulphur in a continuous dead roasting operation upstream of the smelting furnace. Continuous roasting allows for the consistent removal of the sulphur as SO₂ for potential recovery as sulphuric acid. This has obvious environmental advantages over traditional matte smelting. In fact, due to the nature of the DC smelting operation, the primary requirement of the roasting operation in the ConRoast process is simply as a pretreatment of the feed material for removal of sulphur. The intention was to remove as much sulphur as possible, in order to achieve a sulphur content in the furnace feed of less than 0.5% (which is less than the sulphur content of the feed material that Mintek has smelted extensively over the past few years in their DC arc furnace).

With the participation of Hazen Research, Technip developed a pilot testing programme to investigate the critical roasting parameter of sulphur removal from a typical low-sulphur PGM ore concentrate. The primary parameters investigated were: roasting temperature, the use of oxygen-enriched fluidizing air, and excess air ratio. Secondly, the fate of trace elements present in the PGM concentrates was investigated.

Feed material

The feed material chosen for investigation of the roasting parameters of the ConRoast process was a South African

PGM ore concentrate with a nominal sulphide sulphur content of 7.2%. Table I shows the chemical analysis of the concentrate used in this test programme. While it is expected that a typical concentrate such as this would be produced commercially as a filter cake with a relatively high moisture content (approximately 16% moisture), it is not practical to feed such a filter cake to a relatively small pilot unit. Therefore, the concentrate sample was dried, to allow pneumatic feeding to the pilot roaster. Water was metered into the roaster at a rate corresponding to the probable moisture level of the commercial filter-cake feed.

The concentrate contained too little sulphur for autogenous roasting. Additional fuel would therefore be required to maintain the temperatures required for dead roasting. As the initial application of the ConRoast process is intended to take place in southern Africa, coal was chosen as the supplemental fuel. For ease of feeding the coal to the pilot unit, the coal was blended with the concentrate sample for each test condition in amounts corresponding to a theoretical requirement for supplemental fuel for the particular test condition. Coal to concentrate ratios varied from 3% to 7%. The South African coal that was used contained 60% fixed carbon, 17% ash, 23% volatiles, and 0.4% sulphur.

Pilot plant apparatus and test procedures

The apparatus employed for the pilot testing was Hazen's 200-mm diameter fluidized bed roaster. This pilot unit is 200 mm in diameter by 4 m high, and is constructed of 316 stainless steel. The reactor vessel is housed inside a split-shell electric resistance furnace, and the electric heating elements are controlled in three zones. Process gas and entrained solids leaving the fluid bed enter a cyclone for the capture of larger entrained particles. The remaining solids and gases pass through a bag-house for final removal of

Table I
PGM-ore concentrate chemical analysis

Element	Concentration, mass %
Si	19.50
Fe	14.40
Fe ²⁺	4.97
Mg	11.30
S _{total}	7.21
SO ₄ ²⁻	0.81
S ²⁻ (by difference)	6.94
Ni	2.85
Cu	1.89
Ca	1.42
Al	1.20
CO ₃ ²⁻	0.41
C _{total}	0.34
Cr	0.24
Na	0.09
Mn	0.09
Co	0.08
Zn	0.03
Pb	0.01
Pt	92.57 ppm
Pd	42.26 ppm
Se	45 ppm
As	11.5 ppm
Ti	1 010 ppm
Hg	0.28 ppm
Te	<10 ppm

particulates. The bag-house contains four stainless steel sintered metal filters. Solid products are collected in canisters, attached to the cyclone and bag-house, which are emptied on a regular basis.

To initiate the testing, external heating was applied to the fluidized bed reactor by energizing the electrical heaters. When the vessel reached approximately 600°C, the feed for the particular test was started. The oxidation reaction of the feed material with the fluidizing air was exothermic, and the purpose of the external heaters was primarily to compensate for radiant energy losses from the pilot-scale equipment. The operating temperature of the roaster bed was controlled by adjusting the external heater power to maintain the reactor energy balance.

The concentrate feed material was extremely fine in nature and it was expected that the majority of the calcine produced would be entrained and carried from the fluidized bed. Therefore, an inert bed material was maintained in the reactor to act as a thermal sink, allowing the fluid bed to operate in essentially a bubbling bed fluidization regime. The starting bed material was alumina with a nominal size of 356 μm . Approximately 70 kg of starting bed was added to the reactor to attain a 1.5 metre starting bed depth. The same bed material was used for Tests 1 through 14 before being replaced by an olivine material with a nominal size of 500 μm for Tests 15 and 16. (The olivine is a longer-lasting bed medium, as the particles are not as prone to as much wear as competing materials.)

Air or oxygen-enriched air was used as the fluidizing medium. The fluidizing gas entered the bed via a wind-box (plenum chamber) equipped with 'bubble-cap' tuyeres to distribute the fluidizing gas over the cross-sectional area of the reactor. The fluidizing gas to the reactor (including pressure tap and feed-gun purge flows) maintained a

superficial space velocity (SSV) of 0.75 m/s in the bed. The SSV was calculated based on the air metered to the bed zone, adjusted for operating temperature and pressure. The volumetric contribution from water that was injected or present in the feed was not included in the velocity calculations.

Feed blends were prepared from concentrate and coal samples provided by Mintek. The amount of coal blended with the concentrate was based on theoretical energy- and mass-balance calculations that indicated the expected coal requirement to maintain autogenous roasting conditions. A screw feeder was used to meter the concentrate and coal blend to a peristaltic pump. The peristaltic pump provided the positive pressure necessary to pneumatically transfer the feed into the vessel. The feed blend was injected into the bed 165 mm above the air distributor. The roaster exhaust oxygen concentration was controlled by adjusting the feed rate of the concentrate/coal mixture. Water was injected into the bed with an atomizing nozzle to simulate the ~16% moisture expected in the filter-cake feed to a commercial roaster.

Roaster products were collected continuously in canisters attached to the cyclone and bag-house. These canisters were removed periodically and the contents recovered and weighed separately. A sample of the cyclone and bag-house products during the steady-state period for each test was pulled for a semi-quantitative total sulphur analysis using a LECO analyser. These same samples were later quantitatively analysed for sulphur forms. The process exhaust gas from the bag-house was directed through a Venturi and packed-bed scrubber to remove SO₂ from the gas before being exhausted to the atmosphere. A 50% NaOH solution was added to the scrubber water to maintain a pH greater than 9. A draft fan was used to assist in conveying the exhaust gas from the system and to control the pressure in the fluid-bed vessel.

Gaseous products from the roaster were sampled immediately downstream of the bag-house. The gases passed through a chiller to remove moisture, and were continuously analysed for oxygen, sulphur dioxide, carbon dioxide, and carbon monoxide content. Additionally, the fluidizing air was continuously analysed for oxygen content.

Roasting test

Table II shows the matrix of roasting tests conducted, indicating the target conditions, and basic operating results of the tests. The initial test series consisted of a complete matrix of three operating temperatures (850, 900, and 950°C) and four fluidizing air oxygen levels (21, 25, and 30% oxygen by volume). Towards the end of the test programme, higher temperatures and increased oxygen concentrations in the fluidizing air were investigated in further attempts to reduce the sulphur content in the calcined product. Additionally, the effect of increased oxygen content in the exhaust, and the use of olivine as a bed medium were investigated.

Tests 1 through 3 covered the range of temperatures from 850 to 950°C, using ambient air as the fluidizing gas. Exhaust gas oxygen concentration was held between 2.0 and 2.5% oxygen by volume (on a dry basis). Under these conditions, virtually no difference was seen in the total

Table II
Summary of test conditions and results

Test	1	2	3	4	5	6	7	8
Date	21 Aug 2007	22 Aug 2007	22 Aug 2007	23 Aug 2007	23 Aug 2007	23 Aug 2007	24 2007	Aug 2007
Start time	19:00	11:00	17:00	11:00	14:00	18:00	15:00	19:30
End time	22:00	15:00	21:00	13:00	17:00	21:00	18:00	21:30
Duration, min	180	240	240	120	180	180	180	120
Target parameters								
Bed temperature, °C	850	900	950	850	900	950	850	900
O ₂ inlet, (%)	21	21	21	25	25	25	30	30
O ₂ exhaust, (%)	2.0–2.5	2.0–2.5	2.0–2.5	2.0–2.5	2.0–2.5	2.0–2.5	2.0–2.5	2.0–2.5
Process measurements								
Shell temperature, °C	721	780	818	466	519	555	601	634
Bed temperature, °C	852	894	947	849	900	947	859	902
Freeboard temp., °C	834	875	940	834	889	966	863	906
Cyclone temp., °C	NA	433	423	420	454	477	447	425
Baghouse temp., °C	412	408	398	418	428	450	456	485
Fluidizing flow rate, sft ³ /min	12.0	11.2	10.9	11.4	10.8	10.6	11.6	11.3
Water flow rate, kg/h	4.92	4.50	3.66	5.82	5.28	5.29	7.38	7.38
Simulated moisture, (%)	15.6	17.3	16.4	14.4	14.8	14.8	15.9	16.1
Feed rate, kg/h	26.5	21.5	18.7	34.6	29.9	29.9	39.0	38.5
Cyclone capture, kg/h	14.58	11.35	11.60	17.59	18.47	22.38	27.20	14.39
S _{total} , (%)	0.93	0.71	0.71	0.83	0.44	0.45	1.1	0.94
SO ₄ ²⁻ , (%)	2.02	1.82	1.85	1.88	1.06	1.06	1.43	0.86
S ²⁻	0.26	0.10	0.09	0.20	0.09	0.10	0.62	0.65
Baghouse capture, kg/h	4.86	4.24	4.55	6.54	5.49	7.34	4.97	6.54
S _{total} , (%)	1.69	1.98	1.87	1.68	1.38	1.69	2.16	1.1
SO ₄ ²⁻ , (%)	4.84	5.34	5.16	4.52	4.08	4.45	5.8	2.95
S ²⁻ (by difference), (%)	0.08	0.20	0.15	0.17	0.02	0.21	0.23	0.12
Off-gas Composition								
O ₂ , (%)	2.3	2.7	2.4	2.6	2.6	2.7	3.1	2.0
CO ₂ , (%)	6.2	6.5	6.9	7.4	7.9	8.1	9.9	9.9
CO, (%)	476	154	56	477	29	34	720	264
SO ₂ , (%)	5.7	5.3	4.9	7.2	6.5	6.0	11.2	10.0

Test	9	10	11	12	13	14	15	16
Date	24 Aug 2007	27 Aug 2007	27 Aug 2007	28 Aug 2007	28 Aug 2007	29 Aug 2007	30 Aug 2007	30 Aug 2007
Start time	12:00	11:00	14:00	9:30	15:00	13:00	10:30	12:30
End time	14:00	13:00	16:30	11:00	17:00	15:00	11:45	14:20
Duration, min	120	120	150	90	120	120	75	110
Target parameters								
Bed temperature, °C	950	850	900	950	950	1 000	1 000	950
O ₂ inlet, (%)	30	35	35	35	21	21	21	21
O ₂ exhaust, (%)	2.0–2.5	2.0–2.5	2.0–2.5	4–4.5	2.0–2.5	2.0–2.5	2.0–2.5	N.A.
Process measurements								
Shell temperature, °C	578	595	698	770	790	856	852	820
Bed temperature, °C	950	847	898	948	950	997	997	950
Freeboard temp., °C	940	840	986	934	940	988	983	945
Cyclone Temp., °C	397	405	444	429	377	379	294	340
Baghouse temp., °C	418	423	465	427	402	338	279	323
Fluidizing flow rate, sft ³ /min	10.5	11.4	10.8	10.7	10.8	10.2	10.2	10.2
Water flow rate, kg/h	5.28	9.0	8.46	7.38	3.72	3.18	3.18	0
Simulated moisture, (%)	13.1	16.6	16.4	15.7	16.1	13.2	13.3	0
Feed rate, kg/h	35.3	45.9	43.3	39.3	19.2	20.9	20.7	29.0
Cyclone capture, kg/h	18.10	22.24	26.53	30.65	14.55	12.64	18.76	13.66
S _{total} , (%)	0.50	0.57	0.39	0.85	0.76	0.37	0.42	0.32
SO ₄ ²⁻ , (%)	0.93	1.3	0.85	2.12	2.04	0.89	0.98	0.62
S ²⁻	0.19	0.14	0.11	0.14	0.08	0.07	0.09	0.11
Baghouse capture, kg/h	6.54	5.71	5.57	12.63	7.03	5.55	6.77	4.17
S _{total} , (%)	1.6	2.19	1.25	2.06	1.82	0.74	0.79	0.68
SO ₄ ²⁻ , (%)	4.51	5.52	3.47	5.75	4.87	2.19	1.93	1.61
S ₂ (by difference), (%)	0.10	0.35	0.09	0.14	0.20	0.01	0.15	0.14
Off-gas composition								
O ₂ , (%)	2.2	2.1	1.8	2.2	4.5	2.4	2.6	15.9
CO ₂ , (%)	12	10.3	17.0	10.9	6.6	7.9	7.8	5.9
CO, (%)	388	22.5	181	5.1	11.7	47.4	49.7	2
SO ₂ , (%)	10.8	14.3	13.7	12.2	3.7	5.1	5.5	0.4

**Note: The fluidizing flow rate is shown in non-metric units (sft³/min or scfm) as these units are more widely used within Technip.
The 'standard' conditions refer to 70°F and 1 atm.**

sulphur content of the calcine as a function of increasing temperature; however, a clear reduction in sulphide sulphur content of the calcine was demonstrated as roasting temperature increased from 850 to 900°C, and little or no decrease in sulphide sulphur when temperature increased further to 950°C.

Tests 4 through 6 covered the same range of roasting temperatures, using air enriched to 25% oxygen by volume for fluidization. Again, exhaust gas oxygen concentration was targeted between 2.0 and 2.5% oxygen. With the enriched fluidizing air, a slight decrease in calcine total sulphur was seen as a function of increasing temperature. Sulphide sulphur content of the calcine again decreased when the roasting temperature was increased from 850 to 900°C, with no further decrease at 950°C.

Tests 7 through 9 were meant to investigate the roasting results with 30% oxygen in the fluidizing gas. Unfortunately, tests 7 and 8 were plagued by operational disruptions in the feed system, and very little can be gleaned from the results. However, Test 9 at 950°C ran smoothly, and essentially duplicated the results of Test 6, indicating that increasing the fluidizing air oxygen content has much less effect on the total and sulphide sulphur content of the calcine than does increasing temperature.

Tests 10 through 12 looked at a further increase in fluidizing gas oxygen content to 35% by volume. These tests more or less duplicated the results (of total and sulphide sulphur content in the calcine as a function of temperature) that were seen at lower fluidizing air oxygen levels.

Test 13 was intended to look at the effect of increased oxygen content in the roaster exhaust gas (increased excess air ratio). The test was run at 950°C using ambient air for fluidization, with a target exhaust oxygen content of 4.0 to 4.5% by volume (dry basis). The results were not

significantly different from those of Test 3, operated at 2.0 to 2.5% oxygen in the exhaust.

Tests 14 and 15 looked at a further increase in the roaster temperature to 1 000°C. Test 14 showed that a significant reduction in total sulphur content of the calcine is possible by operating at very high roasting temperatures, and that almost total elimination of sulphide sulphur is possible. Test 15 was a duplicate of Test 14, using olivine as the bed medium instead of the granular alumina that had been used for all previous tests. The results nearly duplicated those of Test 14, but showed an increase in sulphide sulphur levels in the range of previous (900 and 950°C) tests.

Finally, Test 16 was conducted to investigate the effect of re-roasting calcine from previous tests at 950°C to determine if further processing of the calcine could further reduce the total and/or sulphide sulphur content. Total sulphur was reduced, but sulphide sulphur remained unchanged, indicating that it was possible to decompose sulphates remaining in the calcine.

Residual sulphur results

The main purpose of the roasting tests was to determine the effectiveness of fluidized bed roasting for removing sulphur from the feed concentrate. Table III shows the results of residual sulphur in the calcined products from the various tests. It was demonstrated that a reduction in sulphide sulphur levels of the calcine occurs when the temperature is increased from 850 to 900°C, and that further reduction of sulphide sulphur at temperatures beyond 950°C does not occur. However, significant sulphate sulphur remains in the calcine at all temperatures ranging from 850 to 950°C. Only when the roasting temperature is increased to 1 000°C, does a significant reduction (decomposition) of the sulphates take place. This is a strong indication that stable sulphates are formed in the calcine during roasting. This is not

Table III
Calcine sulfur results

Test	Temperature (°C)	Inlet O ₂ (%)	S in product (%)	SO ₄ ²⁻ as S in product (%)	S in product (by difference) (%)	Sulphur distribution in calcine, (%) of S as SO ₄ ²⁻
1	850	air, 21	1.10	0.88	0.22	80.2
2	900	air, 21	0.98	0.85	0.12	87.3
3	950	air, 21	1.17	1.06	0.11	90.1
4	850	25	1.13	0.93	0.20	82.9
5a	900	25	0.64	0.48	0.16	74.4
5b	900	25	0.68	0.62	0.07	89.9
6	950	25	0.83	0.70	0.12	84.3
7	850	30	1.27	0.71	0.54	55.9
8	900	30	0.96	0.37	0.54	38.6
9	950	30	0.89	0.73	0.17	82.2
10	850	35	1.02	0.83	0.18	80.8
11	900	35	0.46	0.35	0.10	77.0
12	950	35	1.31	1.17	0.14	89.1
13c	950	air, 21	1.16	1.04	0.11	89.3
14	1 000	air, 21	0.48	0.43	0.06	88.7
15d	1 000	air, 21	0.53	0.42	0.11	79.4
16e	950	air, 21	0.40	0.28	0.12	69.8

^a Sample for higher roaster exhaust O₂ concentration (2.5–3.0%)

^b Sample for target roaster exhaust O₂ concentration (2.0–2.5%)

^c 4.5% excess O₂

^d Olivine bed

^e Olivine bed, Test 3 recycle

altogether unexpected, given the calcium content of the feed concentrate. Calcium sulphate normally requires very high temperatures (1 000°C and greater) for decomposition under oxidizing conditions.

Trace elements

Another aspect of the test program was to investigate the fate of trace elements during roasting. Test 13 roaster products were selected to track the following trace elements: Ir, Rh, Ru, Zn, Pb, Mn, Sb, Se, Au, As, Te, Bi, and V. Test 13 represented a high temperature (950°C) roast with 21% oxygen (air composition) fluidizing air. Table IV shows the trace elements assays for Test 13. A metallurgical balance of the trace elements indicated that all of the trace elements remain with the solid products from roasting (and therefore become part of the smelting furnace feed) with the exception of selenium, for which very little was accounted for in the solid products. Arsenic accountability is notable in that it would normally be expected to volatilize under roasting conditions. However, it appears that the calcine has the capacity to absorb arsenic *in situ*. This is most likely due to the alkali content of the feed concentrate.

Implications for commercial roaster design

The results of the pilot-testing programme indicated the following basic conclusions:

- Fluidized-bed roasting is a viable route for the removal of sulphide sulphur from sulphur-bearing PGM ore concentrates processed by the ConRoast process.
- Low (approximately 0.1%) residual sulphide sulphur levels are attainable by roasting at temperatures 900°C and above without using oxygen-enriched air.
- Oxygen enrichment shows no real advantage in terms of operation or process results.
- Alkaline-earth elements present in the PGM ore concentrates may form stable sulphates, which are difficult to decompose at roasting temperatures below 1 000°C. Roasting temperatures in this range would necessitate special design of refractories, and would have implications for fuel consumption in treating a low-sulphur concentrate. Additionally, the potential for bed agglomeration and other operational problems at temperatures of 1 000°C and above would be of concern.

- Investigation of the tolerance of the smelting operation to the levels of sulphate in the roaster calcine indicated by these tests is warranted.
- Of the trace elements that were tracked, selenium was not accounted for in the solid products of the pilot unit, and may therefore require consideration in the design of commercial roaster exhaust cleaning equipment, for example in the gas-cleaning section of a sulphuric acid plant. Although arsenic appeared to be absorbed in the calcine *in situ*, it should be borne in mind that the trace elements were only investigated in one particular test of one particular concentrate, and that elements like arsenic typically end up in the gas phase of roaster systems to some level.

Conclusions

The roasting testwork clearly demonstrated that it is possible to decrease the total sulphur content of a PGM ore concentrate from 7.2% to as low as 0.3% in the cyclone product, with 0.4% as a weighted average of the cyclone and bag-house products.

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Table IV
Trace element analysis of feed and products from test 13

Element	Units	Feed	Cyclone Product	Baghouse Product
Ir	oz/ton	0.11	0.19	0.14
Rh	oz/ton	0.24	0.30	0.27
Ru	oz/ton	0.39	0.49	0.44
Zn	%	0.27	0.26	0.32
Pb	%	0.01	0.01	0.01
Mn	%	0.09	0.10	0.09
Sb	%	0.00	0.00	0.00
Se	ppm	34.3	0.0	5.0
Au	ppm	3.6	3.8	3.0
As	ppm	4.4	6.9	13.0
Te	ppm	11.0	8.0	10.0
Bi	ppm	0.0	0.0	0.0
V	ppm	91.0	99.0	98.0



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Five years of experience at Hazen Research in Golden, Colorado conducting laboratory and pilot-scale research in the area of thermal processing (roasting, calcining, pyrolysis, and smelting). Seven years of experience at Technip USA in process design of fluidized bed systems for metallurgical and environmental applications.
