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AISI WASTE OXIDE RECYCLING PROGRAM

Final Technical Report

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DISCLAIMER

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EXECUTIVE SUMMARY

In March 1994, AISI completed a five-year, $60 million collaborative development program on Direct Steelmaking cost-shared by DOE under the Metals Initiative. This program defined an energy-efficient and environmentally-friendly technology to produce hot metal for steelmaking directly from coal and iron ore pellets without incurring the high capital costs and environmental problems associated with traditional coke oven and blast furnace technology. As it becomes necessary to replace present capacity, this new technology will be favored because of reduced capital costs, higher energy efficiency, and lower operating costs. The *AISI Direct Steelmaking Program Final Technical Report* was published by DOE as DOE/ID/12847-7 in August 1994.

In April 1994, having failed to move forward with a demonstration plant for direct ironmaking, despite substantial efforts by both Stelco and Geneva Steel, an alternative opportunity was sought to commercialize this new technology without waiting until existing ironmaking capacity needed to be replaced. Recycling and resource recovery of steel plant waste oxides was considered an attractive possibility. This led to approval of a ten-month, $8.3 million joint program with DOE on recycling steel plant waste oxides utilizing this new smelting technology. This highly successful trial program was completed in December 1994. The results of the pilot plant work and a feasibility study for a recycling demonstration plant are presented in this final technical report.

The viability of recycling millions of tons of steel plant dusts and sludges that are now typically landfilled and converting these materials into useful products, i.e., hot metal for steel production, a zinc-rich raw material for the non-ferrous industry, and slag for roadbed or cement production, was demonstrated. Recycling of synthetic electric-arc-furnace dust was also tested. We have shown that steel plant oxides can be smelted in an environmentally and economically sound manner for an attractive return on investment. Specific results are:

- Recovery of Iron. The iron oxides and metallic iron present in steel plant waste oxides were smelted similarly to the hematite and wustite pellets used in the Direct Steelmaking Program. Dust loading from the smelter was less than 6%, and most of the carbon and much of the iron dust in the smelter offgas were recovered in the cyclone and could be recycled to the smelter. The overall iron yield in smelting on a commercial basis will be similar to that for the blast furnace. The hot metal produced was carbon-saturated and lower in silicon and manganese than blast furnace hot metal.

- Recovery of Zinc. The zinc in the waste oxides reported to the sludge with a zinc-to-iron ratio in excess of six. This sludge is a valuable raw material for the zinc industry as verified by Canadian Electrolytic Zinc, Ltd., and other zinc producers.

- Refractories. A unique furnace design, subject of a pending patent application, provides for the formation of a protective frozen slag layer on the inner surface of a stable brick lining. This system consists of special water-cooled copper staves and a combination of refractories, carefully selected for their heat transfer properties, supporting the frozen slag layer. This system will result in heat losses of less than 11% in a commercial-size smelter.

- Energy. The carbon in the waste oxides was used as a fuel/reductant, which resulted in a decrease in the fuel rate. The process offgas has significant fuel value and can be used in steel plants for steam generation or as a partial replacement for natural gas and desulfurized coke oven gas in slab reheating furnaces.

- Environment. Technology was developed to reduce the process offgas sulfur to less than 50 ppm_V when operating with zinc-bearing material. This is less than 5% of the sulfur content in desulfurized coke oven gas. Hot metal desulfurization technology was also developed in the pilot plant to achieve hot metal sulfur comparable to blast furnace hot metal.

- Process Control. The pilot program confirmed and clarified our understanding of the fundamentals of smelting reduction. Process control schemes were developed, tested, and fully demonstrated during the waste oxide recycling trials.

The feasibility study confirmed the design and operation of a plant to process about 500,000 metric tons per year of waste oxides into about 250,000 metric tons per year of hot metal. This involves a fivefold scaleup in size and a threefold increase in pressure (from 0.65 atm. to 2 atm. gage) over the pilot plant. It is about a 2:1 scaleup from the Japan Iron and Steel Federation's DIOS plant at Keihin with whom we have exchanged nonproprietary technical information. The oxygen requirement is about 1100 metric tons per day of 95% purity.

The total project cost for a 500,000 tons/year demonstration project was developed as part of the feasibility study. The capital cost for such a plant would be about $70 million with a profit potential of about $30 million/year, an attractive return on capital once the process has been demonstrated on a commercial basis. We expect that the successful demonstration plant project will lead to construction of six to eight similar recycling plants in the United States.

PILOT PLANT PROGRAM

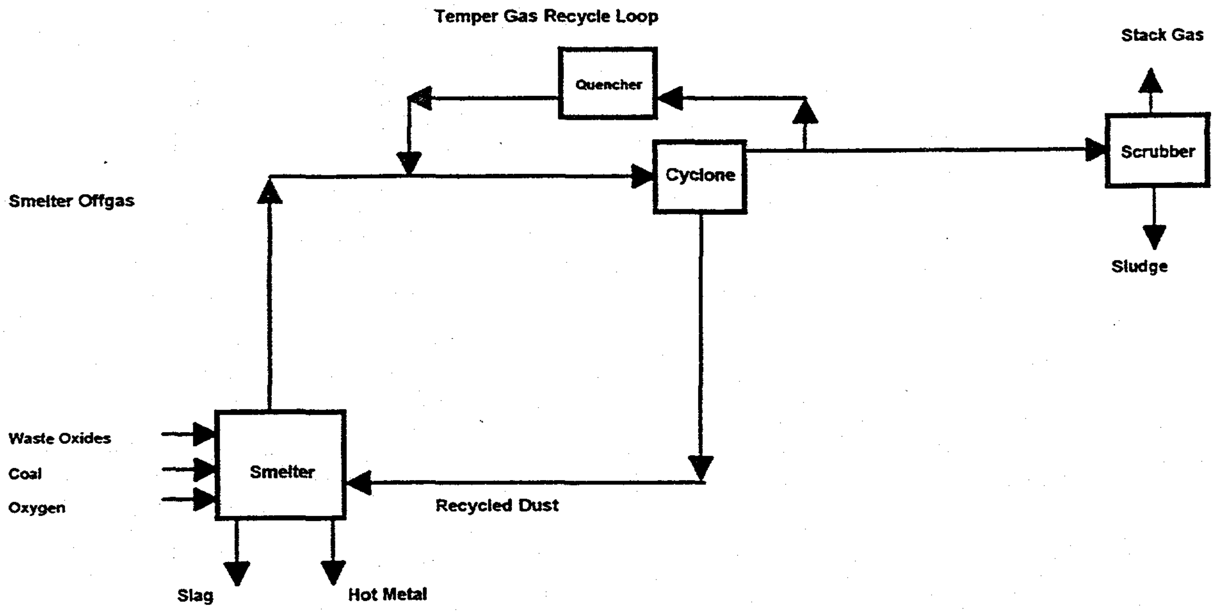
TECHNICAL OBJECTIVES

The main objective of the steel plant waste oxide recycling trials was to demonstrate the applicability of postcombustion smelting technology (developed for direct ironmaking) to the recovery of iron and carbon from these wastes. In addition, the concentration of zinc and lead in a sludge suitable for use by the zinc industry was to be demonstrated. Finally, the information necessary to characterize the process was to be generated.

PILOT PLANT FACILITIES

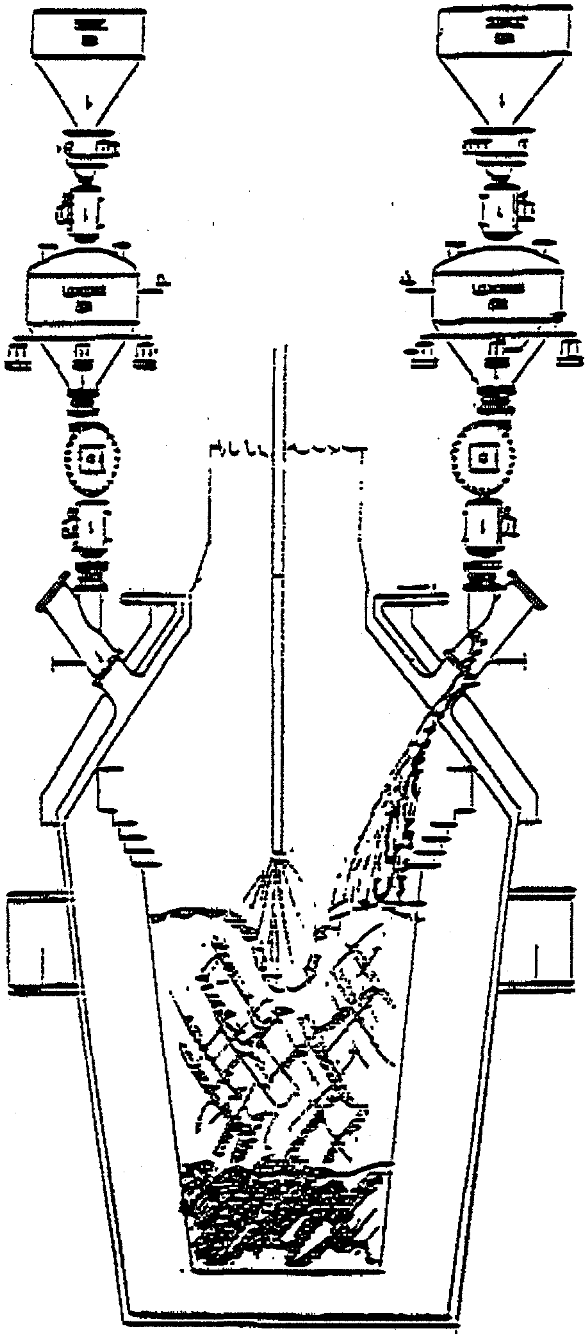
The pilot plant flowsheet is shown in Figure 1.

Figure 1 – AISI-DOE Pilot Plant Flowsheet



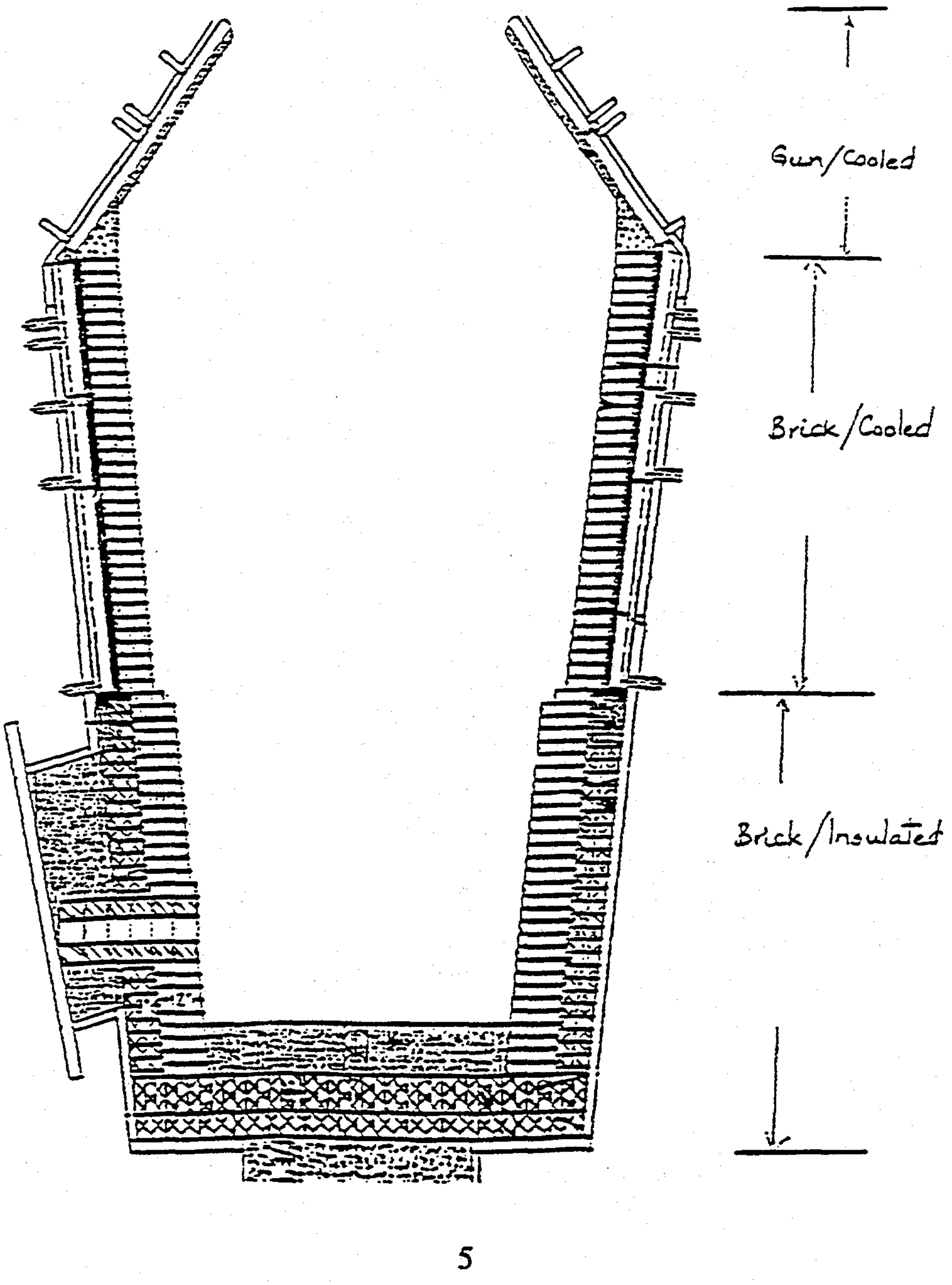
The flowsheet used was the same as that for the direct ironmaking trials. Raw materials such as coke breeze or medium volatile coal, agglomerated waste oxides, hematite pellets, and flux were top charged into the smelter through a double lockhopper arrangement shown in Figure 2. A mix of the top-charged raw materials entered the vessel on diametrically opposite sides. At any given time, material was charged to the vessel from only one feed hopper. Fine materials such as blast furnace dust, BOF dust, and smelter dust were pneumatically injected into the slag. Oxygen was blown in through a dual circuit, water-cooled central lance. Nitrogen flow through tuyeres installed in the floor of the vessel was used for stirring purposes.

Figure 2 – Schematic of the Pressurized Vessel Showing the Feed System



The configuration of the pressurized smelter vessel with the refractory lining is shown in Figure 3. The water-cooled cone and hood (not shown) at the top of the vessel were coated with gunnite material. The vessel was lined with refractory up to the cone. The refractory in the freespace was backed by water-cooled copper panels. After six trials, an outage was taken to extend the water-cooled region into the slag zone. Below the water-cooled region, the refractory brick were backed by an insulating safety lining.

Figure 3 – Schematic of Pressurized Vessel Showing Refractory-lined and Water-cooled Regions



The distance between the barrel-cone interface and the vessel floor was 4.5 meters. The vessel diameters at the floor and the barrel-cone interface were 2.02 m and 3.45 m respectively. The mouth of the cone was 6.17 m above the floor, and the diameter was 1.83 m. The initial set of water-cooled panels extended from 3.28 m (vessel diameter = 3.17 m) above the vessel floor. After additional panels were installed, they began at 1.91 m (vessel diameter = 2.77 m) above the floor. These dimensions are representative of the end of a refractory campaign.

The taphole was located at approximately the fifteen-metric-ton (t)* metal line. Casting was conducted every 90 - 120 minutes. Metal and slag were cast into a "slag box." After the taphole was closed, the metal was poured into "casting boxes." Samples of the metal and slag were taken from the "slag box" and "casting boxes."

A sublance was used to measure metal temperature and slag height and also to obtain slag and metal samples. The metal and slag samples were analyzed during the trial at the pilot plant laboratory. The offgas exiting the smelter was analyzed by a mass spectrometer. The gas samples were obtained from the duct (prior to the cyclone) and from locations after the cyclone. The gas was analyzed continuously for CO, CO_2, H_2, H_2O, N_2, and Ar. A gas chromatograph was used to measure the levels of the sulfur-bearing gases such as H_2S, COS, SO_2, and CS_2. The NO_x and total hydrocarbon contents of the offgas were also monitored.

The gas exiting the smelter was dust-laden as it traveled through the offgas duct. Nitrogen gas, used for purging purposes as well as for raw material charging, mixed with the smelter gas in the duct. In the mixing chamber, prior to the cyclone, smelter gas was tempered by a controlled amount of cold recycle gas. As the tempered offgas passed through the cyclone, some of the dust was removed. This dust was either collected in boxes or reinjected into the smelter after temporary storage in a silo. The dust discharged from the cyclone was sampled at regular intervals. The relatively cleaner gas exiting the cyclone was split into two streams. These streams were quenched separately with the smaller stream being used for tempering the gas entering the cyclone. The sludge from the quenchers was sampled regularly. The gas exiting the main quencher was burned in the flare stack.

The modifications and additions to the pilot plant for the Recycling Program were in three main areas:

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*t is a metric ton and equals 1,000 kg. Metric symbols are used unless otherwise specified.

1. The gas cleaning plant
2. The injection equipment
3. The pressurized smelter vessel cooling system and lining.

Changes to the Gas Cleaning Plant. A significant number of problems had been experienced with the originally installed pressure release "rupture discs," which had opened on several occasions due to hot conditions rather than system overpressure and interrupted continuous operation.

All these discs were removed, and an additional, blast-furnace-type bleeder valve was installed to ensure safety release against overpressure with the ability to return to operation in a short time.

The hot cyclone was modified extensively to increase its ability to withstand higher temperatures and to improve the efficiency. An additional larger man-access door was also installed to facilitate inspection and cleanout, and a water-cooled section was installed at the bottom to help cool garnered particulate.

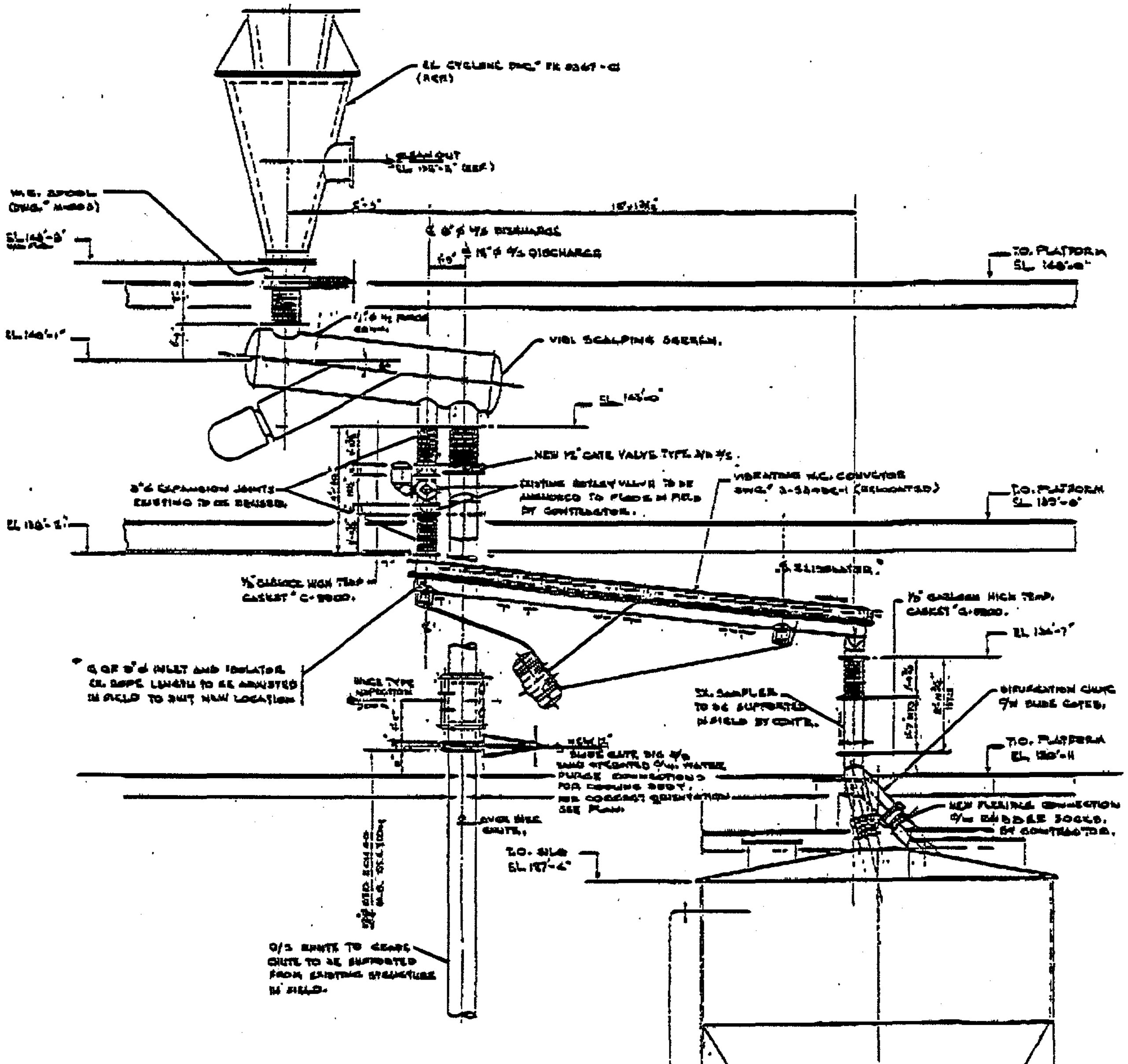
A major change was made to the equipment involved in the extraction of the particulate from the cyclone to eliminate blockage by occasional large pieces. A new water-cooled, high pressure scalping screen was installed immediately under the cyclone, and the vibrating conveyor was relocated downstream from this unit. Changes were also made to allow easier flow of the dust back into the reinjection silo (see Figure 4).

A number of piping and other modifications were also made to the water treatment facilities to improve operational reliability and the flow of slurries.

Changes to the Injection Equipment. One injection unit was rebuilt into a "dense phase" system by replacing one of the existing injection systems with a dense phase system. With appropriate software changes, the system was made operational and used successfully in the experimental trials.

Changes to the Smelter Vessel Cooling System. As the lining of the vessel in the earlier trials had stabilized in front of the water-cooled copper panels installed in the upper part of the vessel and cone at the start of the campaign, it was decided to put an additional row of coolers in the "belly" area of the vessel where the lining had shown serious wear. This involved a complete clean-out of the vessel to the steel shell to permit the installation of the hangers and copper

Figure 4 – Layout of the New Scalping Screen and Cooling Conveyor for the Dust Handling System



coolers and the cutting of numerous holes through the vessel to accommodate the piping to and from the coolers.

An additional booster pump was bought and installed to ensure adequate water pressure to maintain the necessary flow through all the coolers. Appropriate instrumentation was also installed to allow monitoring and control of the cooling water flows and temperature.

After all of the work was completed and pressure tested, the new refractory lining was installed and the vessel was closed again.

Engineering, Construction, and Commissioning Schedule. From the start of detail engineering in April, a seventeen-week time frame was set to completion. This included a five-week shutdown commencing on July 17 to complete the required demolition, the new installation work, and the commissioning.

Long delivery items, such as the scalping screen and the bleeder valve, were ordered early and expedited aggressively to ensure there were no delays. Any advance field work that could be done before the shutdown was undertaken, and a competent construction staff was assembled. The shutdown began as planned, and with the work completed on schedule, the plant was returned to the operations staff by September 1, 1994.

RAW MATERIALS

In the direct ironmaking program, the iron units used were hematite and wustite pellets, and the charging system was designed accordingly. Steel plant waste oxides are much finer materials, and it was not possible to top charge them directly into the smelter using the existing charging system. Therefore, it was decided to use agglomerated waste oxides. The agglomerates, which were top-charged, were prepared by briquetting with molasses and cement being used as the binder. Dry blast furnace and BOF dusts were injected directly into the slag. Anthracite was added to the BOF dust as a flow aid.

Several types of agglomerates were used during the trial program. Tables 1 and 2 summarize the physical and chemical compositions of these agglomerates. The zinc content in the agglomerates was gradually increased over the duration of the trial program. BF dust, BF sludge, BOF dust, BOF sludge, and rolling mill sludge were used to prepare the agglomerates. In integrated steel plants, a mixture of the generated BF/BOF/rolling mill waste oxides can have a zinc content up to about 3.5%. This was the case in agglomerates A, B, C, D1, and D2. In the

EAF-based steel plants, the zinc content in the wastes can be as much as 25%. In agglomerates E1 and E2, the zinc level of EAF plant wastes was simulated by using zinc calcine.

Table 1 – Physical Composition of Agglomerated Waste Oxides

Agglomerate	BF Dust (%)	BF Sludge (%)	BOF Dust (%)	BOF Sludge (%)	Rolling Mill Sludge (%)	Zinc Calcine (%)	Zn level (%)
A	40	40	20	0	0	0	0.67
B	40	20	20	0	20	0	0.7
C	22.5	22.5	20	35	0	0	0.81
D1	25	25	50	0	0	0	1.27
D2	25	25	50	0	0	0	3.48
E1	0	0	70	0	0	30	21.09
E2	15	15	30	0	0	40	24.56

Table 2 – Chemical Composition of Agglomerated Waste Oxides

Agglomerate	A	B	C	D1	D2	E1	E2
Used in Trials	R1, R3	R6	R5	R7, R8	R8-R12	R13	R13, R14
SiO2	7.82	6.41	5.5	6.77	5.58	3.5	4.17
Al2O3	2.11	1.99	2.37	2.2	1.32	0.92	1.05
CaO	13.63	12.78	12.18	18.84	11.73	9.22	8.87
MgO	1.25	1.47	1.35	2.4	1.74	1.39	1.4
FeO	6.18	10.49	9.42	6.92	7.27	5.16	5.04
Fe2O3	49.5	46.87	50.67	44.75	55.7	50.46	39.98
Fe metallic	1.42	0.89	1.21	1.38	1.1	0.79	0.5
Na2O	0.13	0.19	0.27	0.024	0.1	1.11	0.227
K2O	0.53	0.58	0.48	0.13	0.23	0.33	0.281
ZnO	0.83	0.87	1.01	1.58	4.33	26.85	30.57
PbO	0.079	0.082	0.11	0.029	0.023	0.036	0.029
C	15.87	16.19	12.57	10.31	9.61	1.79	6.93
S	0.45	0.43	0.34	0.41	0.31	0.75	1.01
Cl	0.3		0.23		0.14	0.2	0.2
F	0.25		0.25		0.35	0.088	0.15
Total Fe	40.88	41.85	44.01	38.09	45.74	40.13	32.41
Total Gangue	24.81	22.65	21.40	30.21	20.35	15.03	15.49

The fuels used at the pilot plant were coke breeze and medium and high volatile coals. At the conclusion of the direct ironmaking program, it was determined that restrictions in the pilot plant charging system limited the process performance when high volatile coals were used.[1] Further, with the closing of sinter plants and soaking pits, the cost of coke breeze had been reduced and become comparable to that for coal, and from an economic standpoint, the waste oxide recycling process appeared more attractive. For these two reasons, it was decided to use coke breeze for most of the waste oxide recycling trials. A medium volatile coal was used to demonstrate the operability of the recycling process and quantify the process parameters with coal. The compositions of coke breeze and coal are shown in Table 3. Also shown are the compositions of the injected BF dust, top-charged hematite, and fluxes. During the early trials of the program when low zinc-containing agglomerates were used, higher zinc input levels were maintained by charging zinc sinter. The composition of the zinc sinter used is listed in Table 3. Injection of dry BOF dust was conducted using an injection system different from the one used for dry blast furnace dust and high volatile coal. The composition of the injected BOF dust is also shown in Table 3.

Table 3 – Raw Material Chemical Composition

Material	MV Coal	Coke Breeze	BF Dust	Hematite	Zn Sinter	Magnesite	Dolomite	BOF Dust
SiO_2	2.16	4.54	6.69	5.39	7.89	1.77	1	1.88
Al_2O_3	2.3	2.44	1.66	0.29	5.23	0.55	1.63	0.25
CaO	1.07	0.26	5.23	4.89	2.76	1.34	54.47	16.63
MgO	0.13	0.1	1.44	1.65	0.33	95.33	38.5	4.67
FeO			7.63	0.83	1.05			5.92
Fe_2O_3	0.56	1.32	45.37	85.59	8.54	0.97	4.4	59.41
Fe met			1.03	0.72	0.41			0.86
C	83.92	89.12	27.3	0.097	0.026			2.24
S	0.75	0.83	0.35	0.011	0.08			0.067
H	4.61	0.12			0.05			
N	1.33	1.26			0.29			
O	3.17	0						
ZnO					67.75			7.35
PbO					0.36			0.86
Moisture	< 3%	< 3%	<0.5%	5-8%				<0.5%

SMELTER OPERATION

A typical trial began with the charging into the smelter of about 13 t hot metal, melted overnight in an induction furnace. The charging hole was closed, following which an oxygen test was conducted. Thereafter, smelter operation continued until it was decided to terminate the trial. The objectives of the trials were decided in advance, and an operating plan was prepared for each trial.

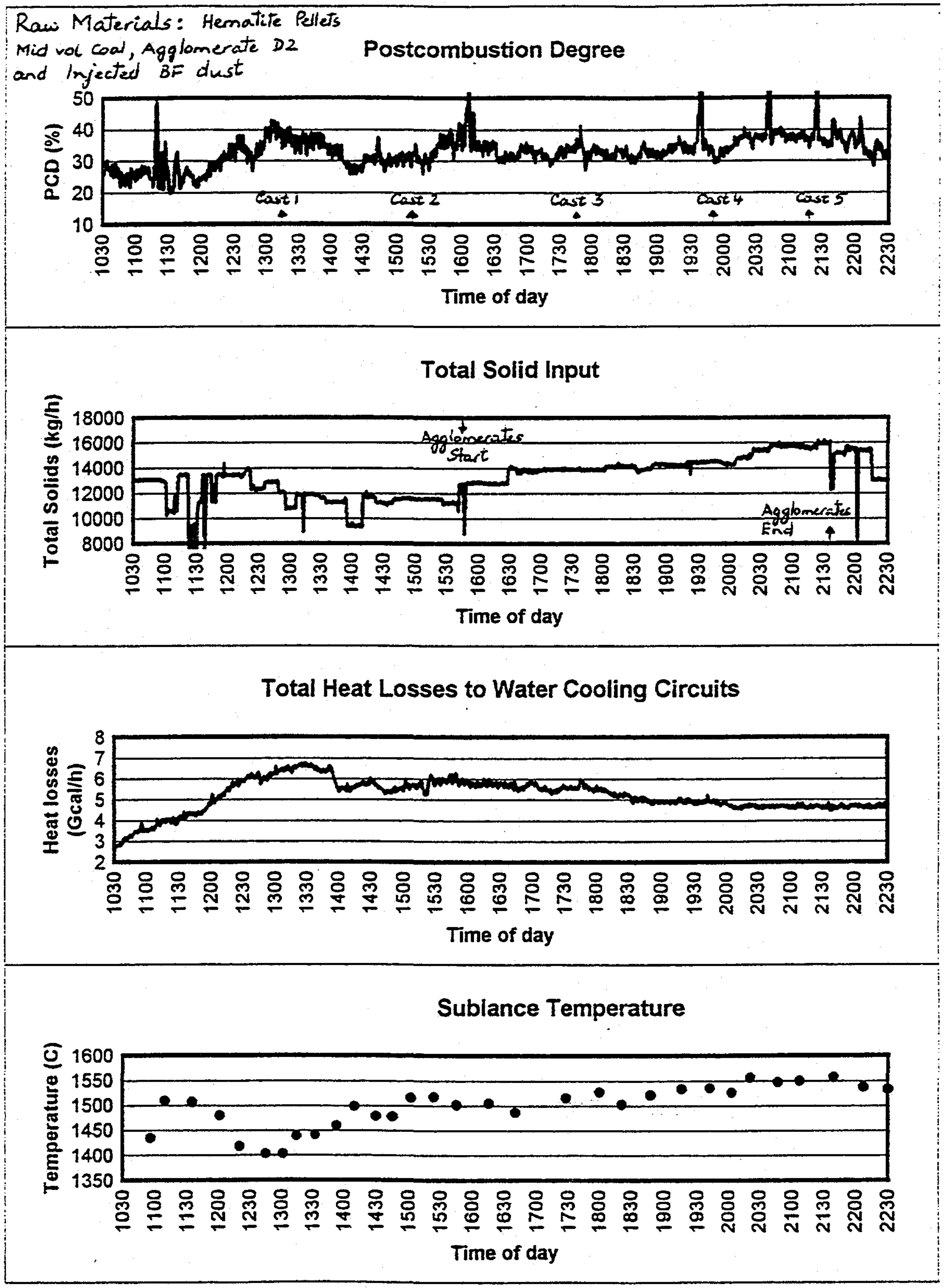
The duration of a trial was typically about twelve hours. The first hour was used for slagmaking, while the next two hours involved the smelting of hematite pellets. By this time, the offgas handling system was sufficiently heated to allow the input of zinc, lead, and alkalis such that their deposition in the offgas ducts and cyclone was not a problem. The smelting of waste oxides (agglomerated or injected) was continued until all experimental objectives were completed and adequate data to characterize smelter operation were gathered. After the addition of waste oxides ended, the smelter was operated with hematite pellets until the "finishing practice" was implemented. The vessel was then drained and allowed to cool before it was inspected.

The technical objectives of each trial were to demonstrate stable operation with the raw materials being used. This primarily implied temperature control which involved postcombustion (PC) control and an understanding of the energy balance. The experimental variables available were the oxygen flow rate, material feed rates, and lance position. After the start-up period, the oxygen flow rate was typically 5500 Nm^3/h. The hematite pellet and waste oxide feed rates were adjusted, based on the energy balance, to maintain a hot metal temperature in the range of 1500 - 1575 °C. The coal/coke breeze addition rate was adjusted based on the PC level and the FeO content of the slag. This control strategy worked successfully, and the process was well characterized by the energy and materials balance.

The vessel, offgas duct, cyclone, and charging system were inspected, and the required measurements and samples were taken after every trial. Samples taken during and after the trial were sent to a commercial laboratory for chemical analysis. The trial results were discussed in posttrial reports.

Example of Smelter Operation. During a trial, several process parameters were measured, and adjustments to the material feed rates, oxygen blowing rate, and lance height were made as required. Figures 5 through 7 illustrate smelter operation when a medium volatile coal was used. Figure 5 shows the PC, total solids input, heat losses to the water-cooling circuits, and the sublance temperature. The PC was above 30% for most of the trial. During the last few hours of the trial, the smelter was operated at a PC level of about 38%. This was accomplished by decreasing the char weight. The sublance temperature is also depicted in Figure 5. As can be seen, after the early part of the trial the temperature was in the 1500 - 1550 °C range.

Figure 5 – Operating Parameters During Trial R12



Raw Materials: Hematite Pellets Mid vol Coal, Agglomerate D2 and Injected BF dust

Cast 1

Cast 2

Cast 3

Cast 4

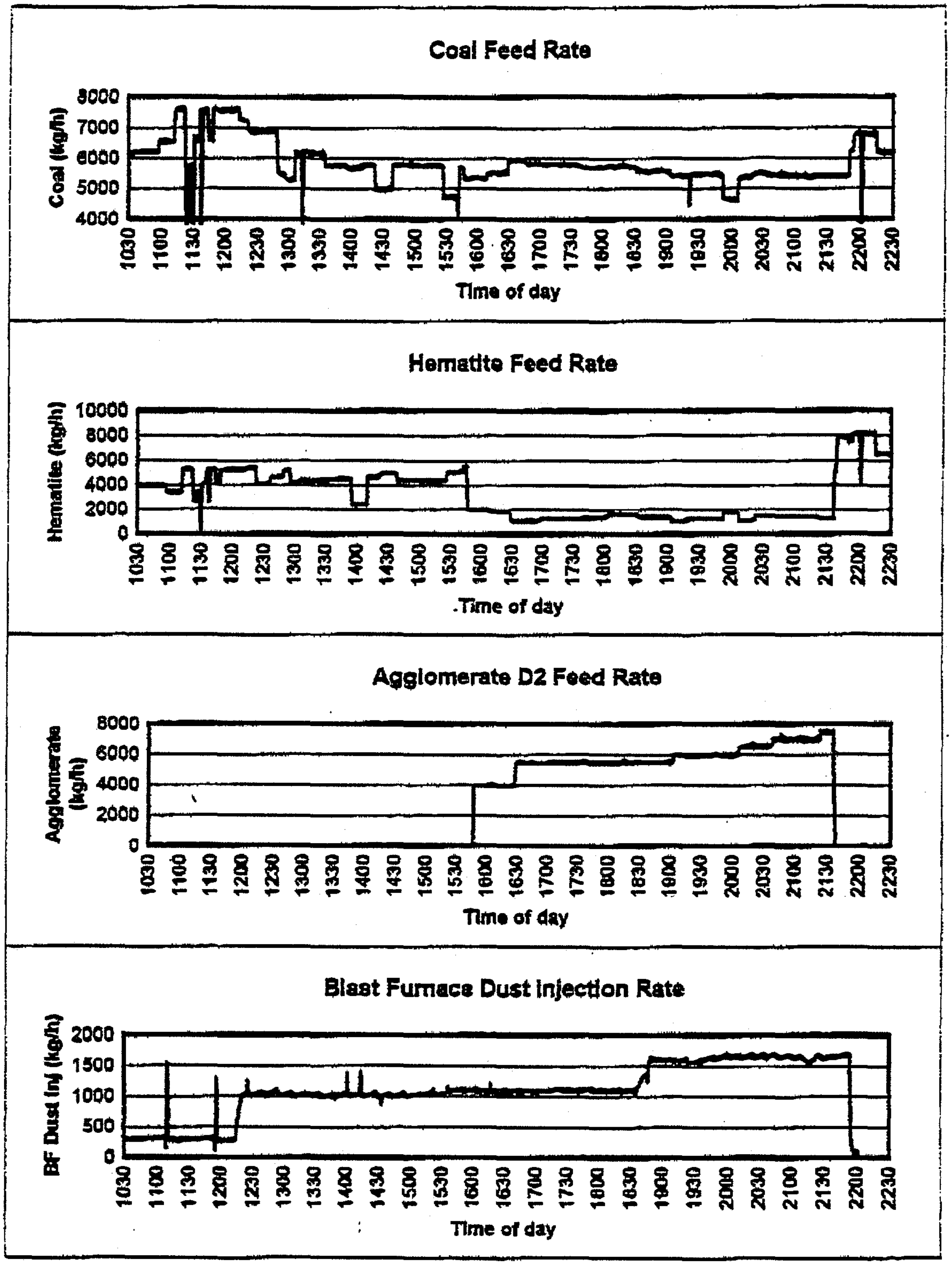
Cast 5

Agglomerates Start

Agglomerates End

Figure 6 shows the raw material feed rates to the smelter.

Figure 6 – Operating Parameters During Trial R12


Coal Feed Rate

Hematite Feed Rate

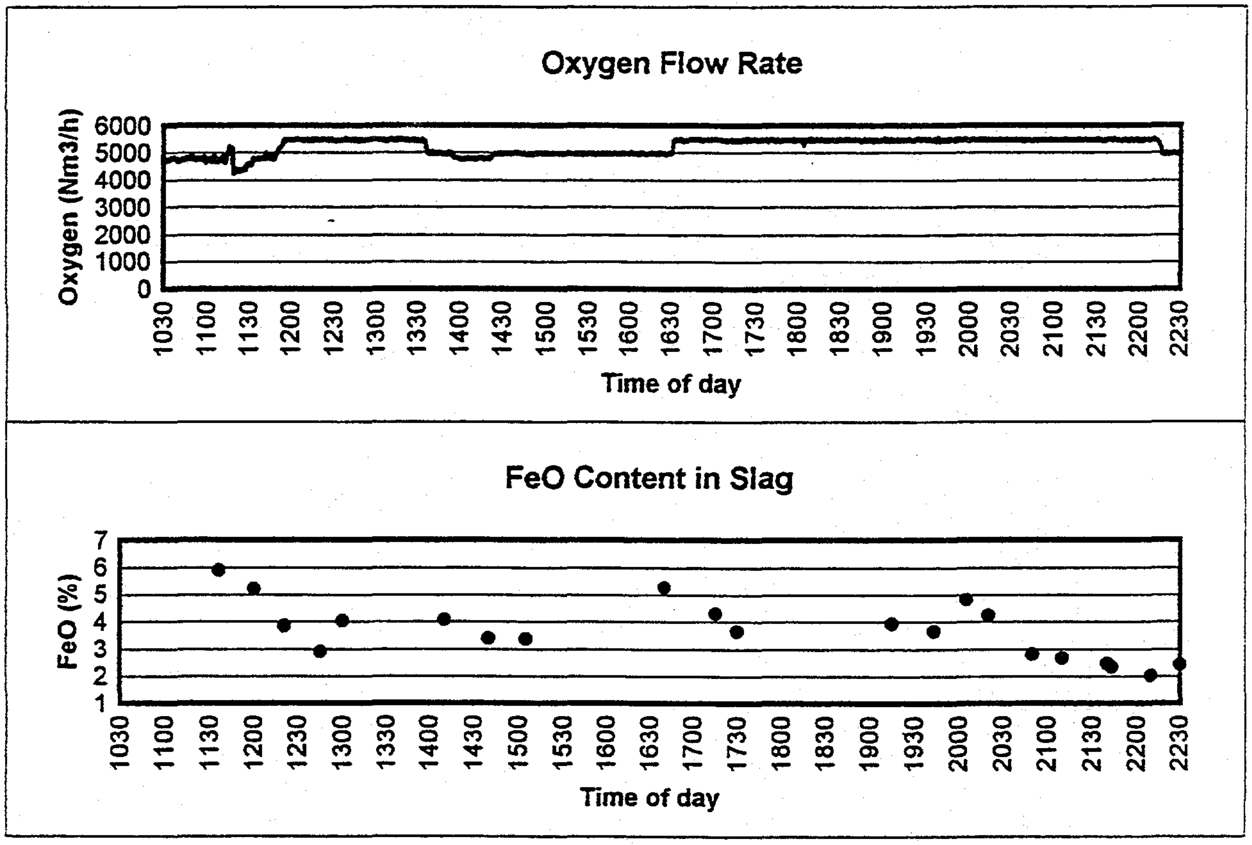
Agglomerate D2 Feed Rate

Blast Furnace Dust Injection Rate

Agglomerate additions began at about 15:45 hours. As the PC level was increased and the heat losses decreased, the agglomerate addition rate and BF dust injection rate were increased in accordance with the energy balance. After it was determined that the trial objectives were accomplished, agglomerate additions were stopped at about 21:40 hours, following which the finishing practice was implemented.

Figure 7 depicts the oxygen blowing rate and the FeO content of the slag. The FeO content of the slag was obtained from slag samples taken by the sublance and was below 6% for almost the entire trial.

Figure 7 – Operating Parameters



The results obtained during the waste oxide recycling trials were reproducible. The main process parameters such as the postcombustion degree, heat losses, offgas temperature in the duct, dust composition and rate, hot metal and slag composition, and the total solids input rate were predictable and reproducible. The process was operated using rigorous energy and materials balances, and the results obtained at the pilot plant conformed to these calculations.

As stated earlier, the trials were about twelve hours long, and the individual operating periods within a trial were up to five hours long. The stability of the operation over that period was considered sufficient to draw interpretive results from the data gathered. In this regard, it is worthwhile to review the issue of the response time of the smelting reactor.

The smelting reactor responds very rapidly to changes made in the operating parameters. The mean residence times for FeO and char in the reactor are of the order of three and 13 minutes respectively. The residence time for the gas is of the order of one second. The process responds to changes in the blowing rate, material feed rates, and lance position in a matter of seconds and reaches stability in a few minutes. The low response time is a result of the enhanced rates of mass transfer and chemical kinetics due to the high temperatures and reactions occurring in the liquid state.

The twelve hours of continuous operation demonstrated the stability of the process, considering the fast response time. Long-term operating reliability of the equipment could not be tested in this mode of operation. However, extensive engineering analysis and the nonproprietary technology exchange with JISF on DIOS have provided assurance on long-term operating reliability.

OPERATING RESULTS

During a trial, several stable operating periods were conducted. These operating periods are characterized by the rate of agglomerate additions, the rate of injection, the type of agglomerate or injected material, the oxygen blowing rate, and initial and final temperature measurements. The operating results for twenty operating periods during the recycling program are shown in Tables 4 and 5. Cases 1 - 5 are for operation with hematite pellets with small amounts of dust injection and/or agglomerate additions. Cases 6 - 8 are for operation with hematite pellets and higher amounts of BF/BOF dust injection. Cases 9 - 20 are for operation with higher rates of agglomerate additions.

In Tables 4 and 5, the trial in which the operating period was conducted is shown along with the time the period started and the length of the period. The type of fuel, agglomerate, and injected material used is indicated in items 5 - 7. The oxygen flow rate and the solid material feed rates are shown in items 8 - 16. The hot metal temperatures measured by the sublance at the start and end of the operating period are shown in items 17 and 18.

Table 4

Table 4 : Recycle Trials - Summary of Operating Results

1	Case Number	1	2	3	4	5	6	7	8	9	10
2	Trial Number	R5	R5	R6	R7	R14	R6	R6	R7	R5	R5
3	Period start time (hrs)	11:04	18:30	15:09	13:40	10:30	20:00	20:58	15:07	13:26	15:39
4	Period length (minutes)	142	88	96	87	180	58	62	106	133	171
5	Top charge fuel type	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze
6	Top charged agglomerate type	None	C	None	None	None	None	None	None	C	C
7	Injected dust type	Smelter	Smelter	BF	BOF	None	BF	BF	BOF	Smelter	Smelter
8	Total oxygen flowrate (Nm3/h)	5509	5510	5501	5481	5449	5487	5499	5479	5605	5474
9	Top charge fuel rate (kg/h)	6278	6069	5933	6188	6232	5792	5060	6081	5363	4476
10	Top charge ore rate (kg/h)	9759	10459	8528	9383	9261	10144	9161	8716	6932	2407
11	Top charge flux rate (kg/h)	691	664	692	692	696	348	682	325	686	560
12	Top charge agglomerate rate (kg/h)	0	498	0	0	0	0	0	0	4239	8230
13	Injected smelter dust rate (kg/h)	262	340	0	0	0	0	0	0	243	247
14	BF/BOF Dust Injection rate (kg/h)	0	0	371	387	0	1213	2421	1933	0	0
15	Total Solid Input (kg/h)	16990	18030	15524	16650	16189	17497	17324	17055	17463	15920
16	Solids/Oxygen Ratio (kg/Nm3)	3.08	3.27	2.82	3.04	2.97	3.19	3.15	3.11	3.17	2.91
17	Metal temperature at start of period (C)	1546	1591	1472	1600	1574	1498	1484	1582	1537	1463
18	Metal temperature at end of period (C)	1537	1536	1535	1582	1538	1484	1485	1553	1463	1591
19	Smelter dust rate (kg/h)	192--413	260--425	570	203--239	377	443--772	441--446	203--457	192--295	264--917
20	Carbon in dust (%)	2--10	1--7	11.13	1.3--2.4	11.6	11--15	16--35	2--5	6--11	4--9
21	Total iron in dust (%)	54--60	25--57	41.4	48--57	41	19--34	29--41	36--48	30--57	25--37
22	Total gangue in dust (%)	7.5--11	7--14	22.4	8--11	15	8--16	11--12	4--11	10--15	13--37
23	Smelter sludge rate (kg/h)	151--249	219--398	251	167--221	173	124--453	122--127	167--443	141--182	182--753
24	Carbon in Sludge (%)	0.3--0.5	0.2--0.5	0.25	0.4--1	0.8	0.5--1.4	0.5--0.6	1--1.6	0.3--0.4	0.3--1
25	Total iron in sludge (%)	57--63	25--58	50.5	47--58	42	7--34	37--40	35--47	24--62	23--37
26	Total gangue in sludge (%)	12--16	5--12	18.6	7--11	14	4--8	9--11	4--11	8--14	11--38
27	Total ZnO in sludge (%)	0--0.5	3--27	4.3	5--10	15	21--54	11--16	10--34	0.4--28	11--27
28	Slag CaO/SiO2 ratio	1.05--1.13	1.33--1.52	1.12--1.22	1.23--1.26	0.98--1.13	1.01--1.34	1.23--1.34	1.09--1.24	1.11--1.2	1.2--1.56
29	Slag FeO (%)	4.08--6.38	2.65--3.22	2.37--4.83	4.22--5.68	0.81--6.56	3.85--3.99	3.98--6.28	3.92--4.5	3.23--4.44	2.25--3.57
30	Hot metal carbon (%)	4.8	4.72	4.89		4.8--4.83	4.55			4.61--4.69	4.92--4.94
31	Hot metal sulfur (%)	0.08	0.06	0.171		0.034--0.15	0.142			.123--.154	.038--.083
32	Measured Postcombustion degree in duct (%)	54.4	53.53	47.87	52.57	52.6	58.49	54	51.89	54.32	47.38
33	Total heat losses to water-cooled circuits (Gcal/h)	3.72	3.23	3.19	4.24	5.05	3.53	2.99	4.7	3.75	3.43
34	System Pressure (kg/cm2 gauge)	0.6	0.58	0.6	0.64	0.6	0.6	0.6	0.65	0.6	0.59
35	Rate of temperature change (deg C/hr)	-3.8	-37.5	39.4	-12.4	-12.0	-14.5	1.0	-16.4	-33.4	44.9
36	Raw hot metal production rate (tph)	5.87	6.54	5.12	5.87	5.36	6.53	6.41	6.22	6.09	5.04
37	Raw slag rate production rate (tph)	2.26	2.4	2.15	2.45	2.26	2.19	2.54	2.36	2.79	2.9
38	Raw fuel rate (kg/t)	1058	918	1158	1055	1163	888	790	979	872	879
39	Carbon from Agglom. and Inj. Oxides (kg/t)	11	22	20	2	0	51	103	8	95	213
40	Oxygen Rate (Nm3/t)	939	843	1074	934	1017	840	858	881	904	1086

Table 5

Table 5 : Recycle Trials - Summary of Operating Results

1	Case Number	11	12	13	14	15	16	17	18	19	20
2	Trial Number	R6	R6	R7	R10	R10	R11	R12	R13	R13	R14
3	Period start time (hrs)	13:44	16:45	17:31	12:59	15:56	17:19	17:28	12:34	15:56	13:30
4	Period length (minutes)	85	174	63	140	79	244	252	202	124	172
5	Top charge fuel type-	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	Coke Breeze	MV Coal	Coke Breeze	Coke Breeze	Coke Breeze
6	Top charged agglomerate type	B	B	D1	D2	D2	D2	D2	E1	E1, E2	E2
7	Injected dust type	BF	BF	None	None	None	None	BF	None	None	None
8	Total oxygen flowrate (Nm3/h)	5442	5447	5476	5449	5373	5458	5479	5477	5464	5474
9	Top charge fuel rate (kg/h)	4172	3269	4775	4914	4984	4508	5490	6020	6015	5617
10	Top charge ore rate (kg/h)	2163	2843	3682	3436	3557	2451	1261	7723	6049	5874
11	Top charge flux rate (kg/h)	326	657	318	558	605	281	241	497	252	357
12	Top charge agglomerate rate (kg/h)	8089	7836	8198	8230	8040	8587	6168	2402	4900	4241
13	Injected smelter dust rate (kg/h)	0	0	0	0	0	0	0	0	0	0
14	BF/BOF Dust Injection rate (kg/h)	353	364	0	0	0	0	1480	0	0	0
15	Total Solid input (kg/h)	15083	14869	16971	17138	17386	15787	14640	16642	17216	18069
16	Solids/Oxygen Ratio (kg/Nm3)	2.77	2.73	3.10	3.15	3.24	2.89	2.67	3.04	3.15	2.94
17	Metal temperature at start of period (C)	1492	1535	1590	1520	1575	1563	1516	1562	1585	1538
18	Metal temperature at end of period (C)	1472	1505	1558	1527	1525	1578	1557	1585	1417	1593
19	Smelter dust rate (kg/h)	540--2025	776--1247	304-722	562--1046	761--2712	833--1210	1034--1293	1097--1146	2211--2700	1850--1998
20	Carbon in dust (%)	5--16	8--14	2	3--16	1--7	4--17	27--48	4--9	3--4	2--6
21	Total iron in dust (%)	33--38	28--37	41--42	21--32	24--31	18--26	11--19	20--28	18--21	10--20
22	Total gangue in dust (%)	19--43	14--28	3--4	3--10	2--5	6--12	6--7.5	4--5	2--5	2--4
23	Smelter sludge rate (kg/h)	221--1708	457--928	277--702	360--1005	558--2509	526--900	485--744	845--884	1859--2447	1455--1857
24	Carbon in Sludge (%)	0.2--0.5	0.7--1.1	1--1.2	1.1--2.2	1--2	1.1--1.4	1.8--2.6	1.3	0.6--0.9	0.9--1.4
25	Total iron in sludge (%)	33--38	30--40	41	20--29	22--30	17--21	17--23	19--24	16--19	9--17
26	Total gangue in sludge (%)	17--46	11--31	2.5--4	2--5	1--2	3--8	3--7	2	1--4	1--2
27	Total ZnO in sludge (%)	2--10	9--13	26--29	43--61	49--58	53--61	42--52	56--66	67--71	62--76
28	Slag CaO/SiO2 ratio	1.07--1.14	1.12--1.44	1.18--1.34	1.28--1.39	1.35--1.46	1.33--1.41	1.22--1.29	1.09--1.2	1.15--1.19	0.98--1.07
29	Slag FeO (%)	2.35--4.3	2.21--4.12	2.58--4.47	1.8--6	2.18--3.71	3.02--4.78	2.48--4.83	3.36--6.63	4.67--4.83	3.36--5.83
30	Hot metal carbon (%)	4.74	4.82--4.9	4.28	4.62	4.9	4.7--4.78	4.87--4.91	4.79	4.61	4.76
31	Hot metal sulfur (%)	0.16	0.095	0.052	0.084	0.038	.104--.116	.038--.127	.138--.145	0.302	0.279
32	Measured Postcombustion degree in duct (%)	45.16	39.92	48.34	56.92	61.33	49.69	34.53	46.73	42.75	47.58
33	Total heat losses to water-cooled circuits (Gcal/h)	3.63	2.96	4.7	4.42	4.1	4.98	4.97	4.73	3.99	4.75
34	System Pressure (kg/cm2 gauge)	0.6	0.6	0.65	0.59	0.54	0.6	0.59	0.6	0.6	0.6
35	Rate of temperature change (deg C/hr)	-14.1	-10.3	-30.5	3.0	-38.0	3.7	9.6	9.8	-81.3	19.2
36	Raw hot metal production rate (tph)	4.48	4.89	5.14	5.64	5.3	4.9	3.7	5.3	4.88	4.44
37	Raw slag rate production rate (tph)	2.56	2.62	3.7	2.99	3.19	2.7	2.3	2.26	2.22	2.27
38	Raw fuel rate (kg/t)	931	668	800	872	940	921	1485	1135	1207	1264
39	Carbon from Waste Oxides (kg/t)	308	273	158	135	140	159	263	8	41	64
40	Oxygen Rate (Nm3/t)	1215	1114	1065	966	1014	1113	1481	1033	1097	1233

The smelter dust and sludge rates and composition are shown in items 19 - 27. The smelter dust is defined as the material leaving the smelter. This includes zinc, lead, and other volatile compounds that may be in the vapor phase when they exit the smelter. The smelter dust rate and composition were calculated from the measured cyclone dust and smelter sludge rates and compositions. Additional information on smelter dust is presented in a later section.

Postcombustion, Fuel Rate, and Productivity

Up to 60% PC was achieved with coke breeze as the fuel source. However, for most operating periods, the aim PC was in the 50 - 55% range. The total solids input rate was about 17 tph, and the hot metal production rate was about 5.9 tph when operating with hematite pellets as the iron-bearing feed. The fuel rate (wet basis) and oxygen rate were about 1060 kg/t and 940 Nm^3/t. The slag production rate was about 2.25 tph.

For operation with agglomerated and injected waste oxides, PC levels of 50 - 55% were demonstrated with coke breeze as the fuel source. The total solids input rate was also about 17 tph. However, the hot metal production rate was lower at about 5 tph, while the slag production rate was higher at about 3 tph. The fuel rate (wet basis) was lower, while the oxygen rate was higher.

As stated earlier, the agglomerates were prepared by briquetting using cement as the binder. The binder comprised about 10% of the agglomerate. This resulted in the agglomerate having a lower iron and carbon content and a higher gangue content. These issues are reflected in the lower hot metal production rate and the higher slag production rate. Nevertheless, it can be concluded that the iron oxides present in the waste oxide were smelted and the iron was recovered.

The lower fuel rate obtained during operation with waste oxides was due to the presence of carbon in the waste oxides. The fact that the fuel rate was lowered demonstrates that the carbon in the waste oxides was used as a fuel/reductant.

For operation with a medium volatile coal, an average PC of 34.5% over a five-hour period was demonstrated. The PC in the last couple of hours was raised to about 38% by decreasing char. When operating at 38% PC, with coal, the total solids input rate was similar to that for operation at 50% PC with coke breeze.

Injection of the recycled dust from the cyclone, blast furnace dust, and BOF dust into the slag was successfully conducted in several trials. Injection rates of up to 2.5 tph were achieved with

BF and BOF dust. Under appropriate operating conditions, blowthrough of the injected waste oxides did not occur, and this was confirmed by the measured dust and sludge rates.

Smelting of synthetic EAF steelmaking waste oxides was also successfully demonstrated. Zinc inputs in excess of 1 tph were used, and the results showed that zinc and lead reported to the sludge.

As stated earlier, the hot metal production rate when operating with hematite pellets was about 6 tph. The vessel volume up to the barrel-cone interface was about 24 m^3, resulting in a production intensity of 6 t/(m^3 day). In the case of the direct ironmaking flowsheet, the iron feed to the smelter is preheated wustite. This reduces the thermal requirements in the smelter, and production intensities in excess of 8 t/(m^3 day) can be achieved. This level of production intensity is more than three times that of the blast furnace.

In summary, it can be said that the postcombustion smelting technology developed for the smelting of hematite and wustite pellets was used to smelt steel plant waste oxides. The iron oxides present were reduced to produce hot metal, while the carbon present in the waste oxides was used as a fuel/reductant. The smelting of injected waste oxides was successfully demonstrated. The zinc and lead present reported to the sludge. Zinc-to-iron ratios in the sludge in excess of six, as required by the zinc producers, were obtained.

Heat Utilization and Thermal Efficiency

The heat losses and heat fluxes to the vessel walls were well quantified by direct measurement of the refractories and the gas temperature and the temperature increase in the water-cooled circuits. The results with respect to the heat losses, heat fluxes, thermal efficiency, and heat transfer are presented below.

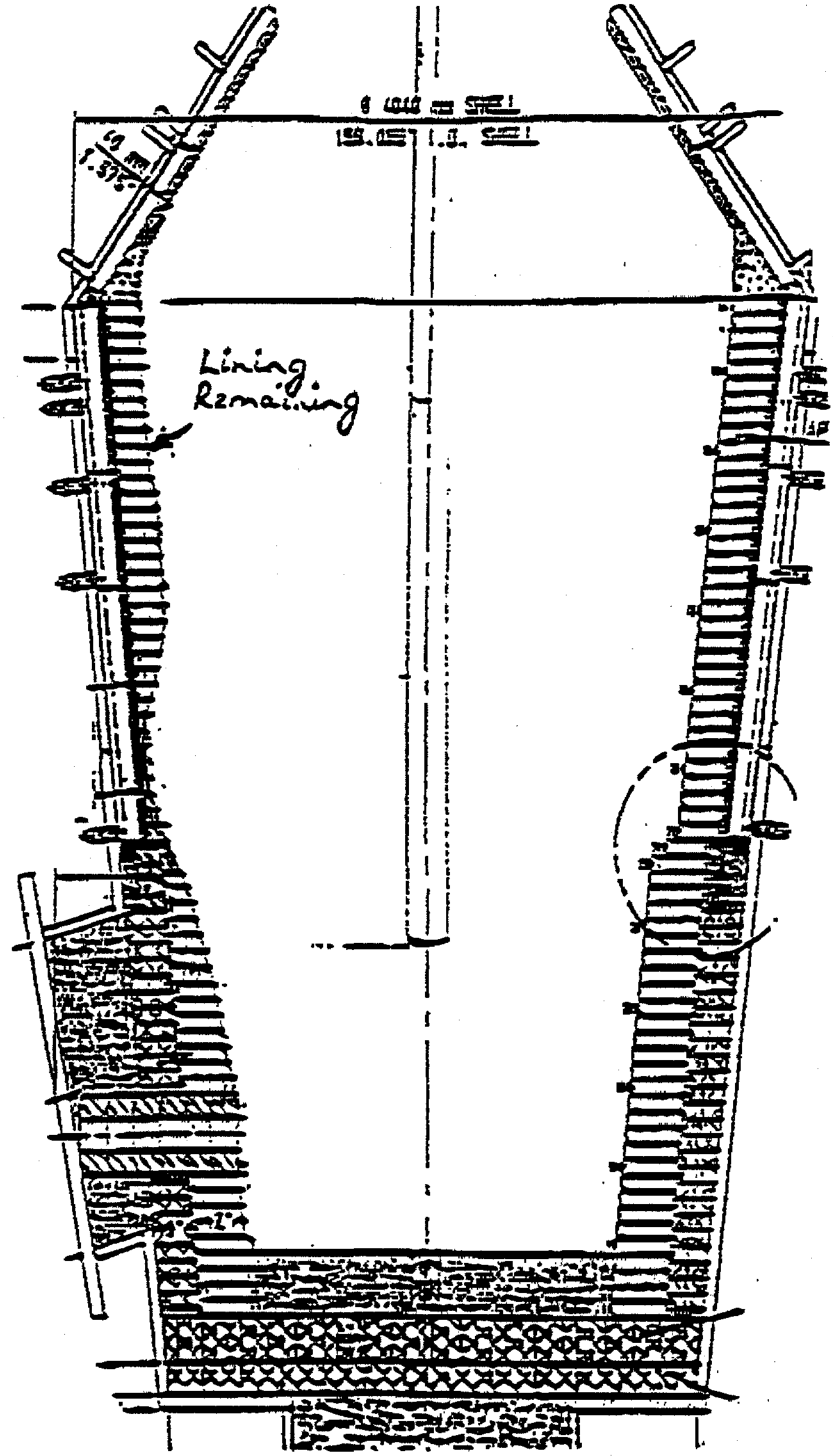
Table 6 lists the heat fluxes and losses to the various regions in the smelter vessel. The heat fluxes to the refractory, barrel and belly coolers, and cone were estimated based on the exposed surface area in each zone. The vessel dimensions, which were used in calculating the areas of the individual regions, were presented in the pilot plant equipment section. The diameter of the lance was 27.3 cm, and the exposed length was 5.53 m.

In Table 6, results for operation with and without the belly coolers are shown. For the case with belly coolers, the total heat losses to the refractory, barrel/belly, cone, and lance were 3.6 - 4.7 Gcal/h as compared to 3.1 - 4.2 Gcal/h for operation without belly coolers. The increase in heat losses was about 0.5 Gcal/h. This is consistent with that calculated from a heat balance using actual temperature measurements. The heat flux to the barrel was estimated to be 0.04 - 0.05 Gcal/(h m^2) when the water-cooled portion was in the free space. After the panels were lowered, the estimated heat flux increased to about 0.06 Gcal/(h m^2). This was due to the refractory wear in a narrow band in the upper slag (shown in Figure 8) such that the panels were exposed to slag.

Table 6 – Heat Losses and Heat Fluxes to Different Regions in the Smelter

Without Belly Coolers			
Region	**Heat Loss (Gcal/h)**	**Area (m2)**	**Heat Flux Gcal/(h m2)**
Refractory	0.9-1.2	30.35	0.03-0.04
Barrel	0.5-0.6	12.77	0.04-0.05
Cone	0.9-1.2	15.4	0.06-0.08
Lance (at 3 m)	0.8-1.2	4.8	0.17-0.25
	3.1-4.2		
With Belly Coolers			
Region	**Heat Loss (Gcal/h)**	**Area m2**	**Heat Flux Gcal/(h m2)**
Refractory	0.5-0.7	17.8	0.03-0.04
Barrel + Belly	1.4-1.6	25.52	0.055-0.063
Cone	0.9-1.2	15.4	0.06-0.08
Lance (at 3 m)	0.8-1.2	4.8	0.17-0.25
	3.6-4.7		

Figure 8 – Wear Profile at End of Campaign After Trial R11



At the pilot plant, heat losses to the water-cooled hood played a crucial role during operation. These heat losses varied from 0.5 Gcal/h to 2.5 Gcal/h, depending on the thickness of material coating them. Much of the contribution to the hood heat losses was from direct radiation as opposed to heat transferred from hot gases. It is important to consider these radiation losses when designing the smelter hood and offgas cooling system.

The total heat generated in the smelter during the waste oxide recycling trials was about 21.5 Gcal/h. This heat consists of contributions from the combustion of C to CO and CO and H_2 to CO_2 and H_2O. The heat required for vaporization of moisture, reduction reactions that are endothermic, and raising the temperature of the produced hot metal, slag, offgas, and dust to the operating temperature is about 17 Gcal/h. Previous work[1] has shown that the heat transferred to the smelter did not correlate to the cross-sectional area of the vessel. The correlation obtained between the heat transferred and the total slag volume suggests that heat transfer scales up volumetrically rather than scaling up with the reactor cross-sectional surface area. The heat losses to the refractories, lance, barrel, belly, cone, and hood are about 4.5 Gcal/h with the resulting offgas temperature being equal to the hot metal temperature. Thus, the thermal efficiency of the process was about 80%.

The offgas from the smelter has substantial chemical and sensible heat. The sensible heat is lost as the offgas cools through the ducts and is quenched. The chemical heat is recoverable, although this was not demonstrated at the pilot plant. The chemical heat content of the offgas after quenching, for operation with a mid vol coal, is about 200 BTU/scf.

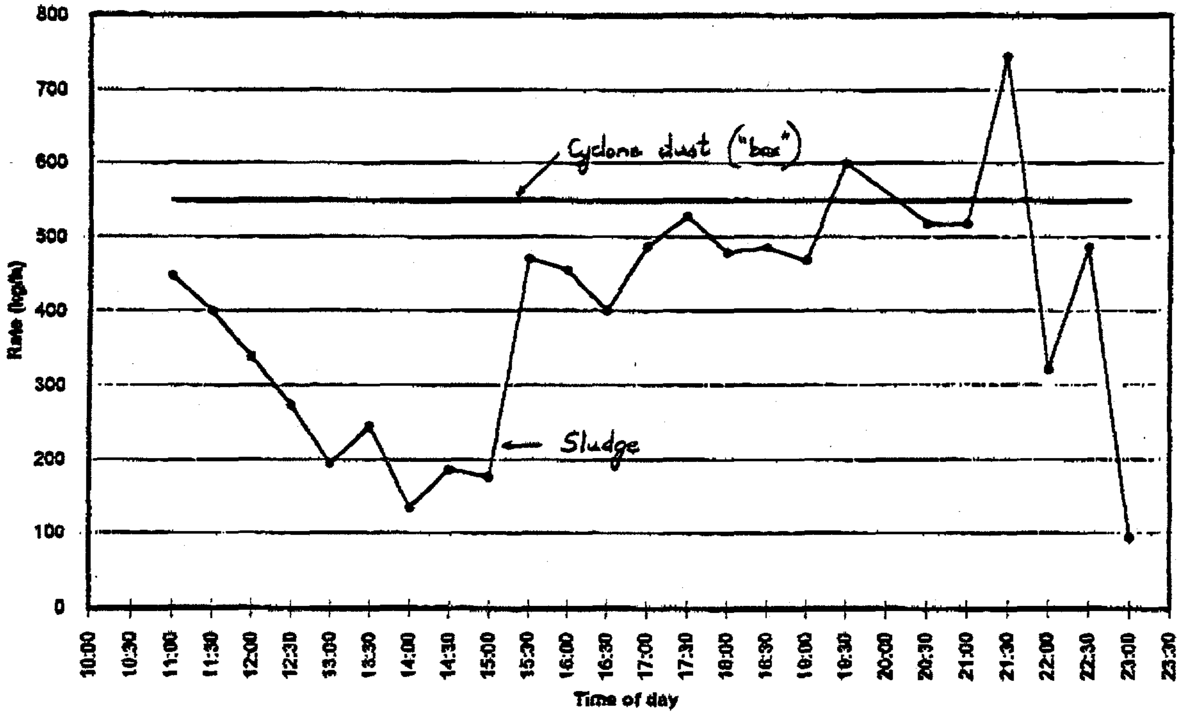
The following conclusions can be drawn. The heat fluxes and heat losses at the pilot plant were quantified. The additional heat loss with the belly coolers was about 0.5 Gcal/h. The heat losses to the refractory in contact with slag/metal are affected by the metal and slag temperature. The heat losses to the hood are from radiation and must be minimized by appropriate design. This will result in improved thermal efficiencies. Consequently, for a fixed oxygen blowing rate, the production rate will increase and the fuel rate will decrease. A very good correlation between the heat transfer and total slag volume was obtained, implying that heat transfer scales up volumetrically rather than with the vessel cross-sectional area.

Smelter Dust

The offgas exiting the smelter was dust-laden. Part of this dust was captured in a dry form by the cyclone. The dust bypassing the cyclone was collected as sludge. Samples of the cyclone catch, water, and solids were collected. Since the rate of water flow was known, the sludge rate could be estimated from the dry weight of the solids and the total weight of the samples.

Figure 9 illustrates the cyclone dust and sludge rates measured. The rate was obtained by weighing the dust collected over the entire trial ("box"). In estimating smelter dust generation, the rate obtained from the box samples was used. In trials R5, R7, and R14, dust from the smelter was not collected in boxes, and in these cases, the cyclone dust rate was determined from the "grab" samples; however, these measurements were considered less reliable.

Figure 9 – Cyclone Dust and Smelter Sludge Rates Measured During Trial R12



As shown in Figure 9, the sludge rate decreased from 11:00 hours to about 13:00 hours, i.e., the start-up period of the trial. This was typical of all trials and was due to lack of adequate slag cover. As the slag weight was increased, the sludge rate decreased due to lower iron losses. After 15:00 hours, the sludge rate increased from about 200 kg/h to 500 kg/h. This was due to agglomerate additions and the zinc charged to the system. Zinc reported to the sludge, causing the sludge rates to increase. Oxygen blowing stopped at 22:58 hours, and the sample taken at 23:00 hours showed much lower sludge rates. At 23:15 hours, dust discharge into the boxes had stopped.

Figure 10 depicts the amount of smelter dust as a percent of material inputs. The closed circles represent trials with coke breeze, while the open circles stand for the mid vol coal trial. The smelter dust is defined as the sum of the cyclone dust and smelter sludge. The data shown consider only those trials in which the cyclone dust was collected in boxes.

The total smelter dust increases with increasing zinc oxide input. This is because zinc is not retained in the smelter. For operation with hematite pellets alone, the smelter dust was about 3% of the total solid input when coke breeze was used as the fuel source. With mid vol coal as the fuel source, the total smelter dust was about 6.25% of the total solid input. With agglomerate additions, the zinc and lead input increased the dust accordingly.

The non-zinc dust was calculated by subtracting the zinc oxide content from the total dust. The non-zinc dust as a percent of the total solid input is plotted for operation with coke breeze and mid vol coal. As shown in both instances, the values were in a relatively narrow range. For coke breeze, the non-zinc dust was about 2 - 4% of the total solids input, while for coal it was 5 - 6%.

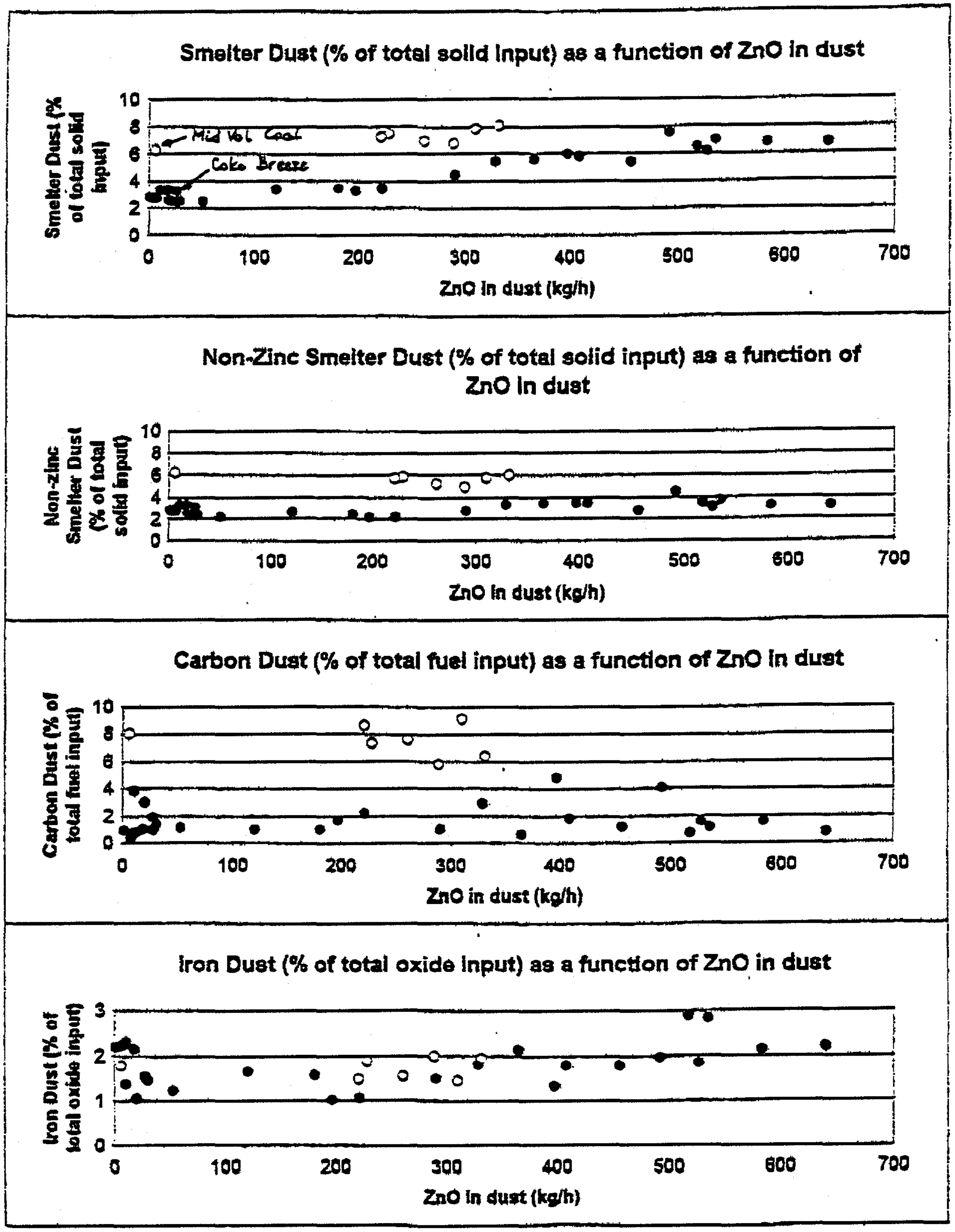
Carbon dust is also shown as a percent of the fuel input. The carbon dust ranged from about 6 - 9% of the mid vol coal input and was mostly less than 2% of the coke breeze input. The carbon contained in the agglomerated or injected waste oxides was not considered as part of the total fuel input in this estimation. If this were taken into account, the carbon dust, when operating with waste oxides, as a percent, would be lower by up to 30% of the values shown.

When operating with coke breeze or mid vol coal, the amount of iron in the dust is less than 2% of the total oxide input (see Figure 10).

At the pilot plant, the cyclone catch was not always reinjected into the smelter. In a commercial operation, this will be done, and much of the carbon and part of the iron will be recovered.

The amount of carbon and iron in the dust appears to be independent of the zinc input.

Figure 10 – Smelter Dust, Carbon, and Iron Dust as Percent of the Material Inputs



Mechanism of Dust Formation. The following observations and discussion are based on the results of the waste oxide recycling trials and the direct ironmaking trials.[1]

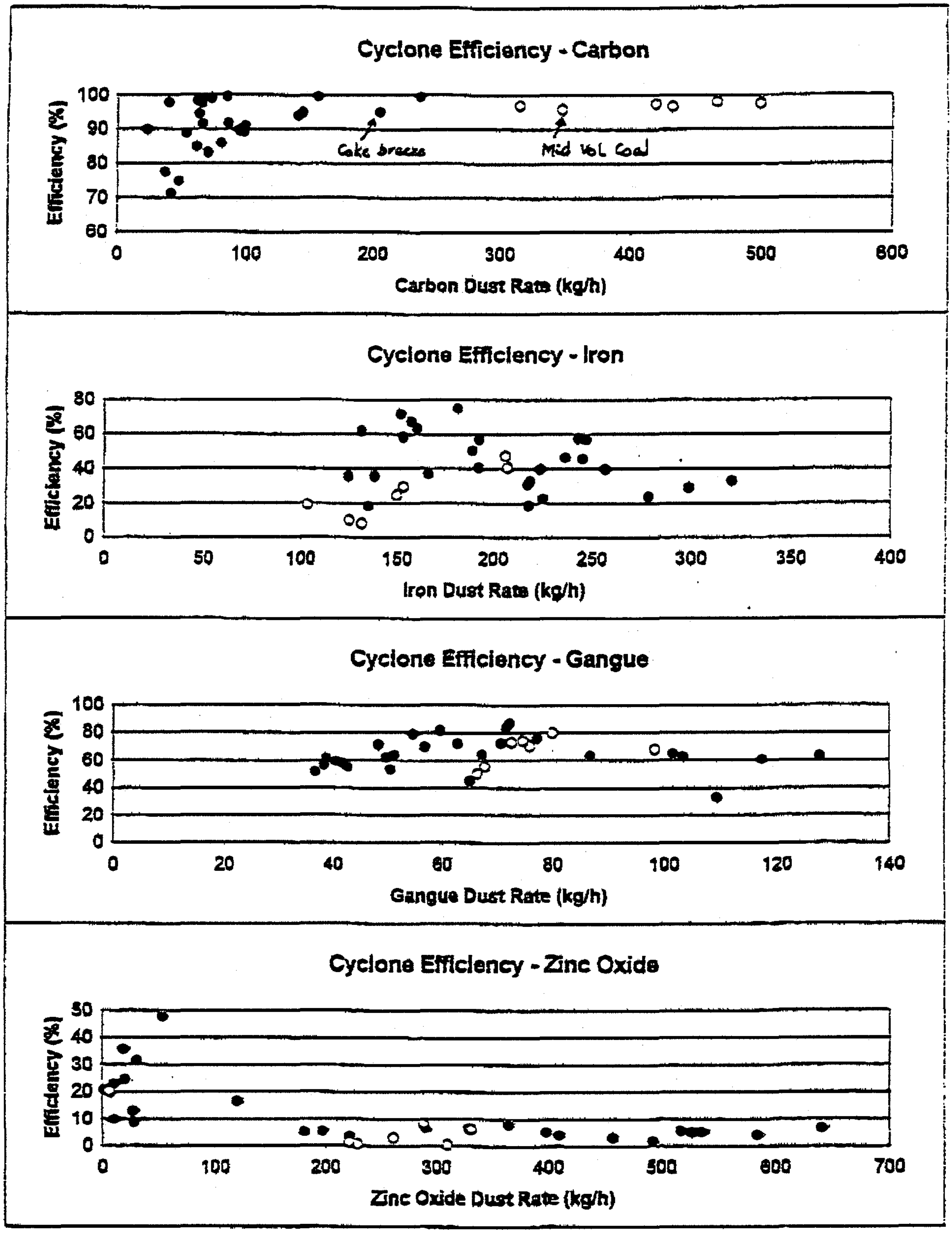
The amount of dust increased significantly with increasing volatile matter content of the coal. The increase was primarily due to additional carbon losses. The carbon losses could not be explained by entrainment of fines alone. It is known that, during coal devolatilization, fragmentation of the coal particle can occur. This will result in the production of additional fines that may be carried out of the smelter. In addition, carbon from the volatiles may be carried out of the reactor as soot.

There was a substantial amount of metallic iron present in both the dry cyclone dust and wet sludge. The amount of slag present in the smelter and the lance position affected the iron dust. The effect was rather substantial after a heavy slag cast, at low lance heights, and during startup of the smelter. Microscopic analyses of the cyclone dust and sludge have shown the presence of micron-sized metallic iron particles, some of which have an outer iron oxide covering. The sludge was almost 100% finer than 500 mesh (25 microns). Finally, the iron-to-carbon ratio in the sludge was almost always more than 100 when operating with only coke breeze and hematite. The above information suggests that the iron dust from the smelter primarily comes from vaporization or fuming of iron.

Cyclone Efficiency. Figure 11 shows the cyclone efficiency with respect to carbon, iron, gangue, and zinc oxide.

The cyclone is highly efficient for carbon removal. For operation with mid vol coal, the cyclone captured more than 95% of the carbon dust. With respect to iron, the cyclone efficiency varied substantially between 20% and 80%. For gangue (CaO, SiO_2, MgO, Al_2O_3, and other slag compounds), the efficiency of the cyclone was mostly 60 - 80%. The cyclone throughput for zinc oxide was over 90%.

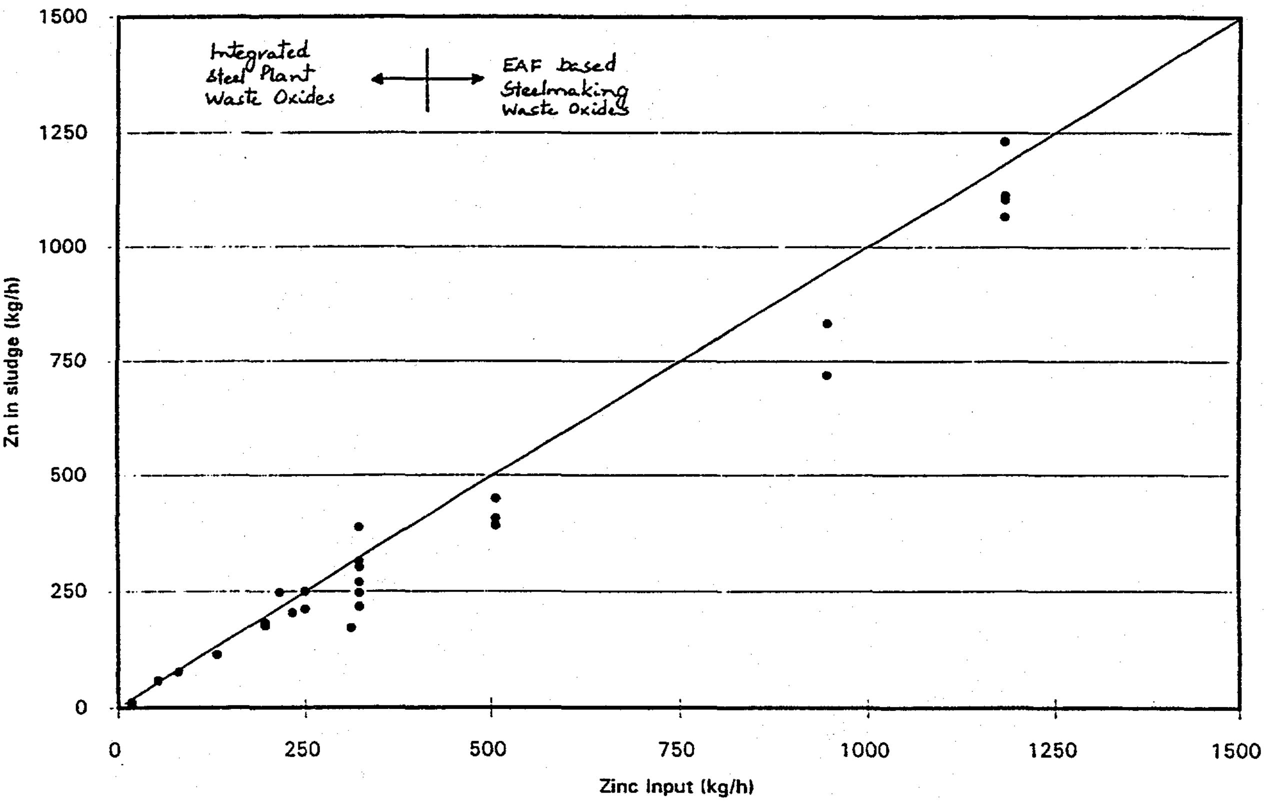
Figure 11 – Cyclone Efficiency for Carbon, Iron, Gangue, and Zinc Oxide



Zinc Recovery

The pilot plant trial data (see Figure 12) show conclusively that about 95% of the zinc in the charge material reported to the sludge, while less than 5% reported to the cyclone dust. With recycling of the cyclone dust to the smelter that will be done in a commercial operation, this minor amount of zinc will also ultimately report to the sludge.

Figure 12 – Zinc in the Sludge as a Function of Zinc Input to the Smelter



This sludge, which on a dry basis might contain about 60% zinc, is a potential raw material for the zinc industry. The value of this material to the zinc producers depends on the amount of impurities it contains, principally as iron, alkalis, and halides. The minimum acceptable zinc-to-iron ratio depends on the specific flowsheet at the zinc plant and may vary between 5:1 and 10:1. The pilot plant tests showed that, with appropriate process control, the amount of iron in the dust was independent of the amount of zinc in the smelter feed and could be kept to less than 200 kg/h in most cases (Figure 13). It was further concluded that vaporization of iron or iron fuming is the predominant mechanism by which iron entered the offgas stream and, as such, can be controlled by maintaining good foaming slag cover, applying soft oxygen blowing practices, appropriate lance height practices, and avoiding excursion of excessively high smelter temperature. Actual zinc balances for Trial 12 are shown in Figure 14. Similar balances for lead are also included in the same figure. The transfer of zinc and lead to the water system was not observed, and their levels in the contact water over the entire recycling trial program were never above 1 ppm.

Figure 13 – Iron in the Sludge as a Function of Zinc Input to the Smelter

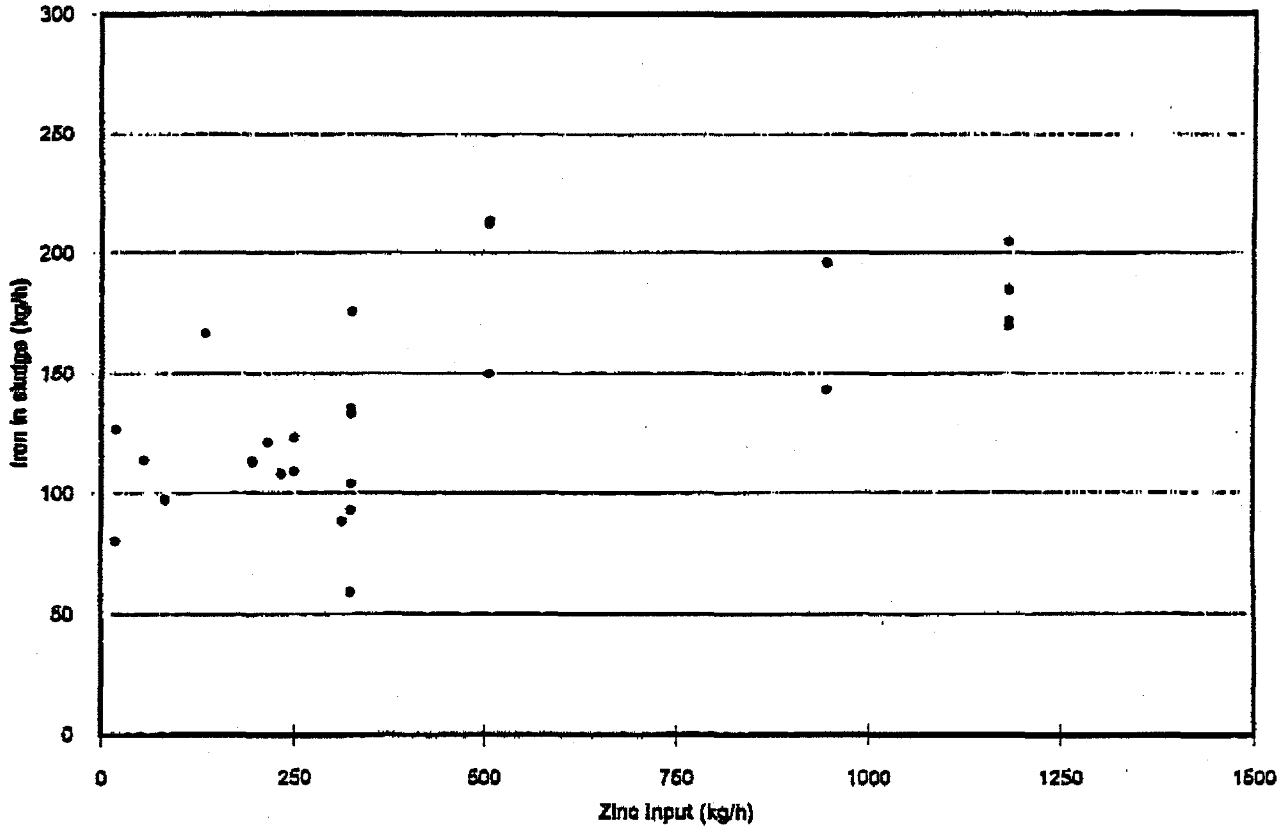


Figure 14 – Mass Balances for Zinc, Lead, Potassium, and Sodium

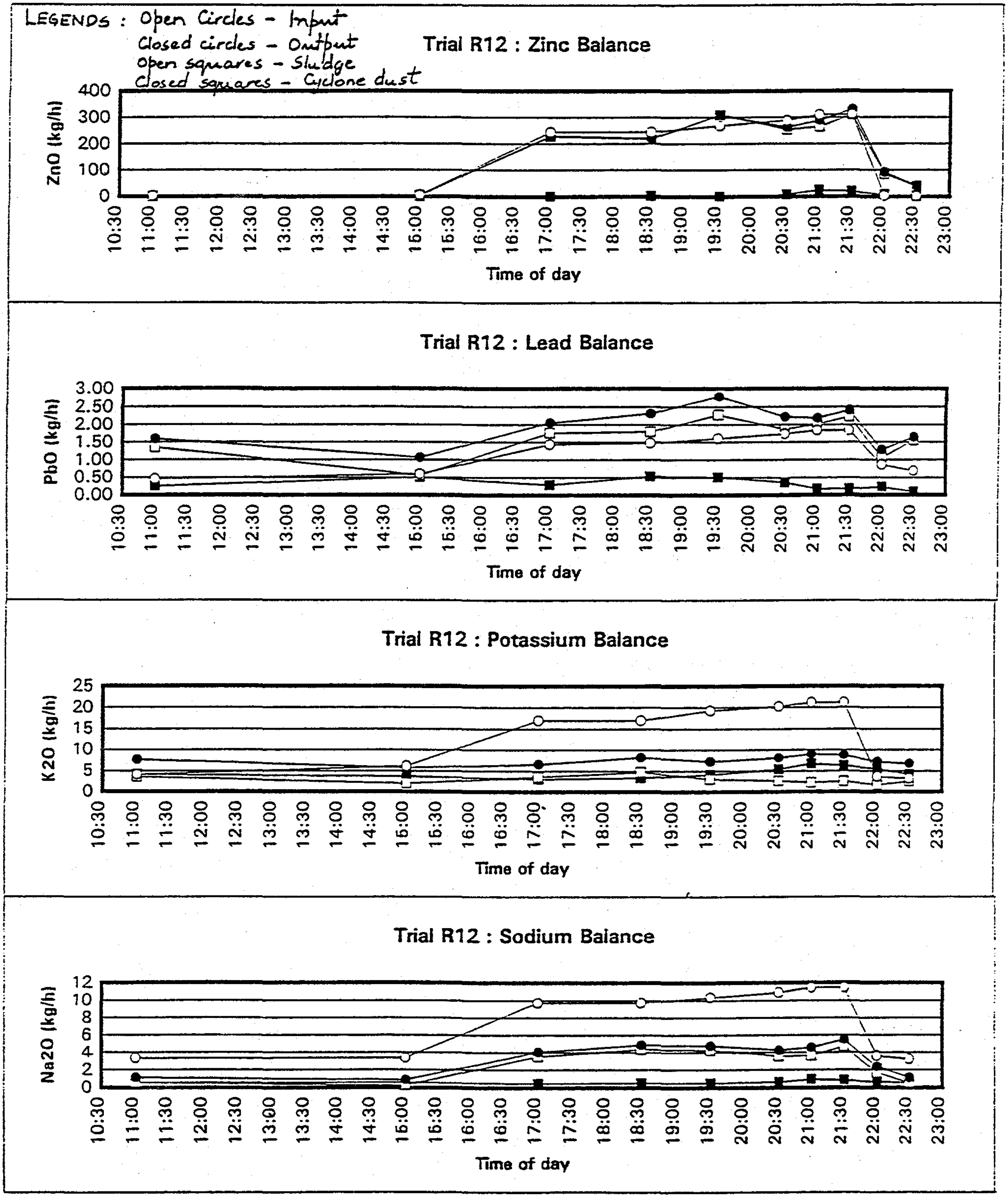
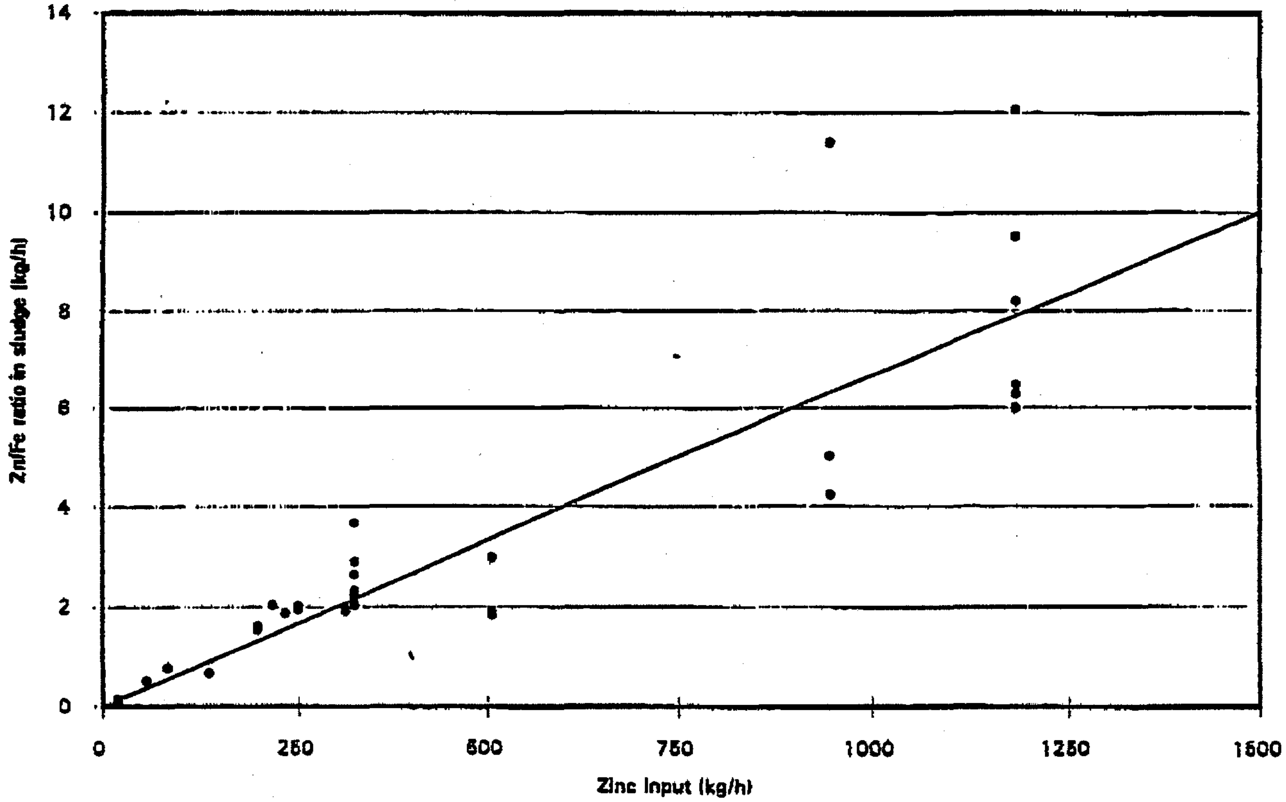


Figure 15 depicts the zinc-to-iron ratio in the sludge. For situations akin to those for integrated steel plants, the zinc-to-iron ratio was less than four. At higher zinc loads, as in waste processing for EAF-based plants or for integrated steel plants with smelter sludge recycling, zinc-to-iron ratios in excess of six and up to twelve were achieved. The solid line represents the expected zinc-to-iron ratio for a baseline iron sludge rate of 150 kg/h, and specific practices were developed to assure that zinc-to-iron ratios in excess of five can be observed. Sludge samples from the pilot plant have been evaluated by Noranda Technology Center (NTC), on the basis of which the sludge has value as a raw material to the zinc plants.

Figure 15 – Zinc-to-Iron Ratio in the Sludge As a Function of Zinc Input to the Smelter



Sulfur Management

Sulfur is introduced into the smelter mainly with coal/coke breeze, waste oxides, and to a small extent, the recycling of cyclone dust. The input sulfur distributes itself between the hot metal, slag, cyclone dust, smelter sludge, and tail gas. The amount reporting to the hot metal determines the extent of hot metal desulfurization required, while the amount present in the tail gas affects the need for gas desulfurization.

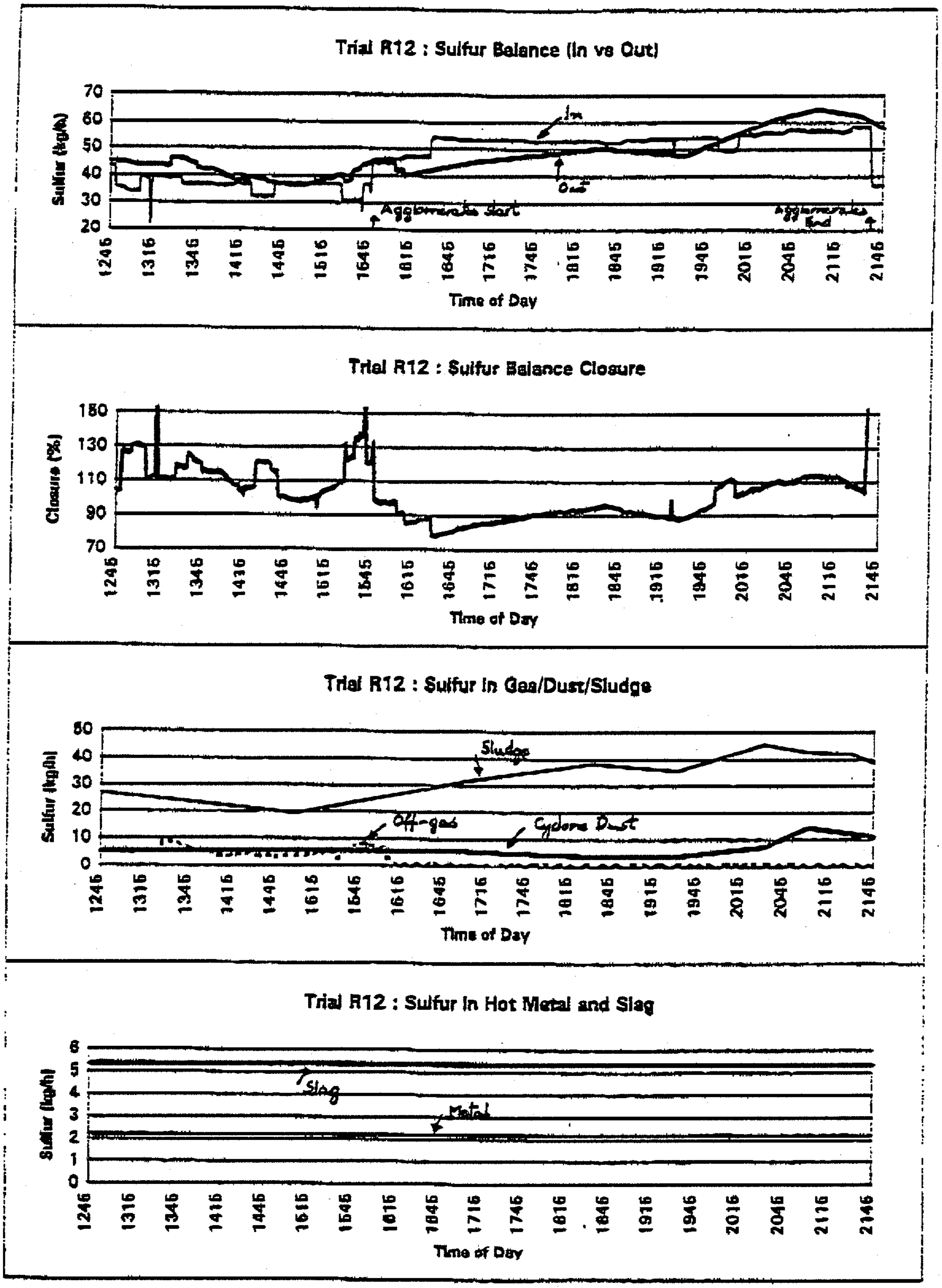
Sulfur Distribution. Mass balances for sulfur were conducted using data gathered over several hours of stable operation. The results are summarized in Table 7.

Table 7 – Summary of Sulfur Mass Balances

Trial #	Period Time		Length	Sulfur In	Sulfur Out	Closure		
	Start	End	(hours)	(kg)	(kg)	(%)		
R6	12:55	20:55	8	463.34	469.98	101.43		
R10	12:15	15:15	3	183.64	162.93	88.72		
R12	12:45	21:45	9	425.13	430.55	101.27		
R14	11:45	17:45	6	462.65	397.81	85.99		
Trial #	Sulfur Distribution based on Input (%)				Sulfur Distribution based on Output (%)			
	Metal &	Cyclone	Smelter	Gas	Metal &	Cyclone	Smelter	Gas
	Slag	Dust	Sludge		Slag	Dust	Sludge	
R6	31.35	16.77	47.89	5.42	30.91	16.5	47.2	5.3
R10	22.11	11.3	54.02	1.33	24.88	12.73	60.89	1.5
R12	16.06	12.99	67.27	4.96	15.85	12.82	66.42	4.9
R14	32.32	6.68	45.54	1.45	37.58	7.76	52.96	1.69

Closure over the entire operating period considered ranged from 86 - 101%. Figures 16 and 17 illustrate the mass balance calculations.

Figure 16 – Sulfur Balances, Closure, and Distribution During Trial R12


Trial R12 : Sulfur Balance (In vs Out)

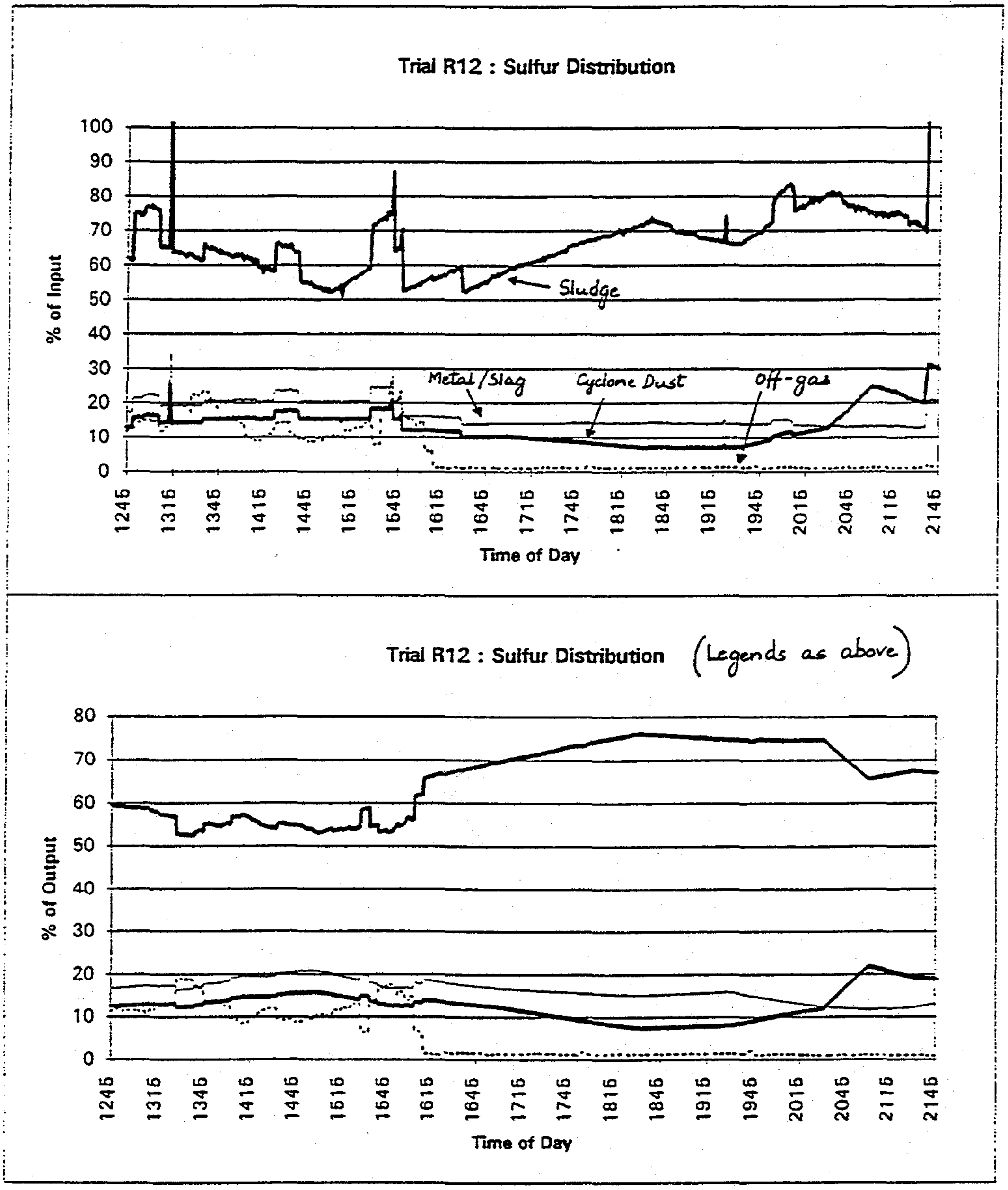
Trial R12 : Sulfur Balance Closure

Trial R12 : Sulfur in Gas/Dust/Sludge

Trial R12 : Sulfur in Hot Metal and Slag

Figure 17 shows the distribution of sulfur between the cyclone dust, sludge, offgas, and hot metal/slag. The instantaneous closure for the sulfur balances ranged between 70 - 130%. Considering the small amount of sulfur input (less than 0.5% of the total solid input), sampling, and chemical analysis issues, the degree of closure obtained was deemed to be satisfactory and led to the following interpretation of the results.

Figure 17 – Sulfur Distribution During Trial R12



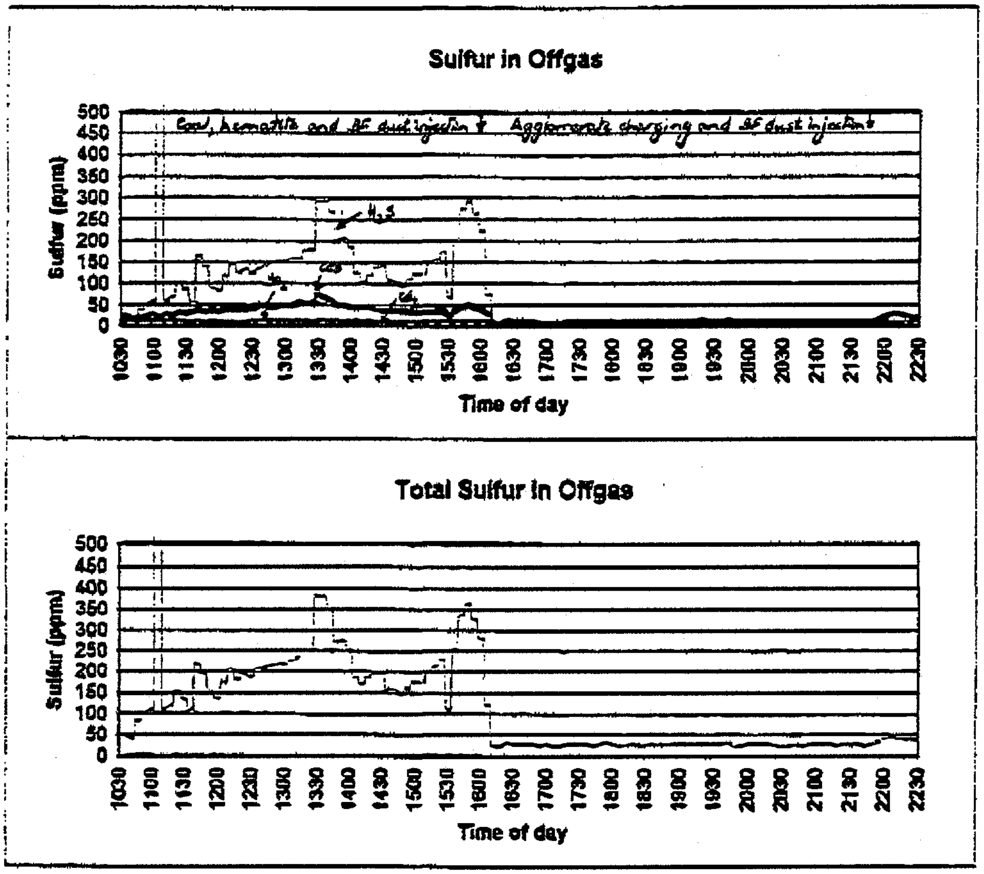
Most of the sulfur input reported to the smelter sludge. This was the case even when operating with hematite pellets alone. About 50 - 70% of the sulfur input reported to the sludge. The fraction of sulfur reporting to the condensed phases (metal and slag) was about 15 - 35%.

The hot metal and slag sulfur levels varied, depending on the lime-to-silica ratio and FeO content of the slag. Less than 15% of the input sulfur was present in the cyclone dust.

The initial hours of operation were conducted with hematite pellets. After the temperatures in the gas handling system were stable, agglomerated waste oxides containing zinc were charged into the smelter.

During operation with hematite pellets as the only iron-bearing feed, the sulfur (equivalent H_2S) content of the offgas, with coke breeze as the fuel, ranged from 75 ppm$_V$ to 250 ppm$_V$. With mid vol coal as the fuel, the sulfur (equivalent H_2S) content of the offgas varied between 100 ppm$_V$ and 350 ppm$_V$ as shown in Figure 18.

Figure 18 – Sulfur in Offgas During Trial R12

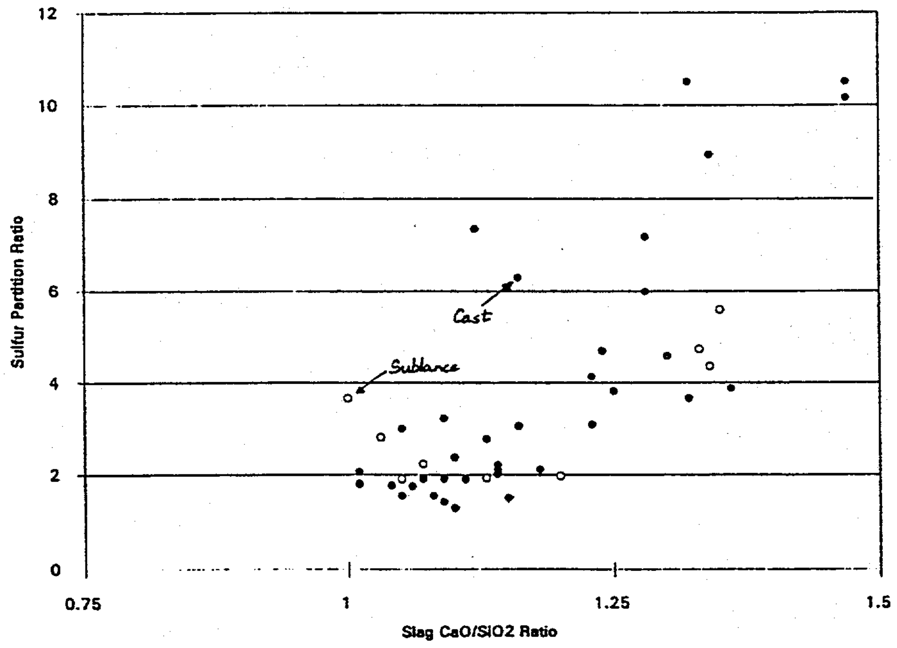


Charging of zinc-containing agglomerates dramatically reduced the sulfur content of the offgas. In most cases, the offgas sulfur (S) content decreased to a stable concentration in less than 30 minutes to less than 50 ppm_V. This is up to 300 ppm_V lower than when operating with hematite pellets alone. To remove an additional 300 ppm_V from the smelter gas, about 15 kg/h or 0.15% of zinc in the iron-bearing material is required on a stoichiometric basis. At the pilot plant, several different zinc-charging rates were used. The offgas sulfur level could be reduced to below 50 ppm_V by ensuring that the iron-bearing feed contained the appropriate amount of zinc. This compares to about 900 ppm_V sulfur in desulfurized coke oven gas and confirms that zinc is an extremely good gas desulfurizer. The fraction of the input sulfur reporting to the offgas was less than 20% when operating with hematite alone. With zinc-containing agglomerated waste oxides, the fraction of sulfur reporting to the gas was less than 2%.

<u>Hot Metal Sulfur at Tap</u>. During trials with hematite and waste oxides similar to integrated steel plant situations, the hot metal sulfur content, samples from the casting boxes, ranged from 0.04 - 0.17%. In trials R13 and R14, when agglomerates made by using zinc calcine were charged, the hot metal sulfur was as high as 0.3%. This resulted from the agglomerates containing 1% sulfur due to the high sulfur content in the zinc calcine.

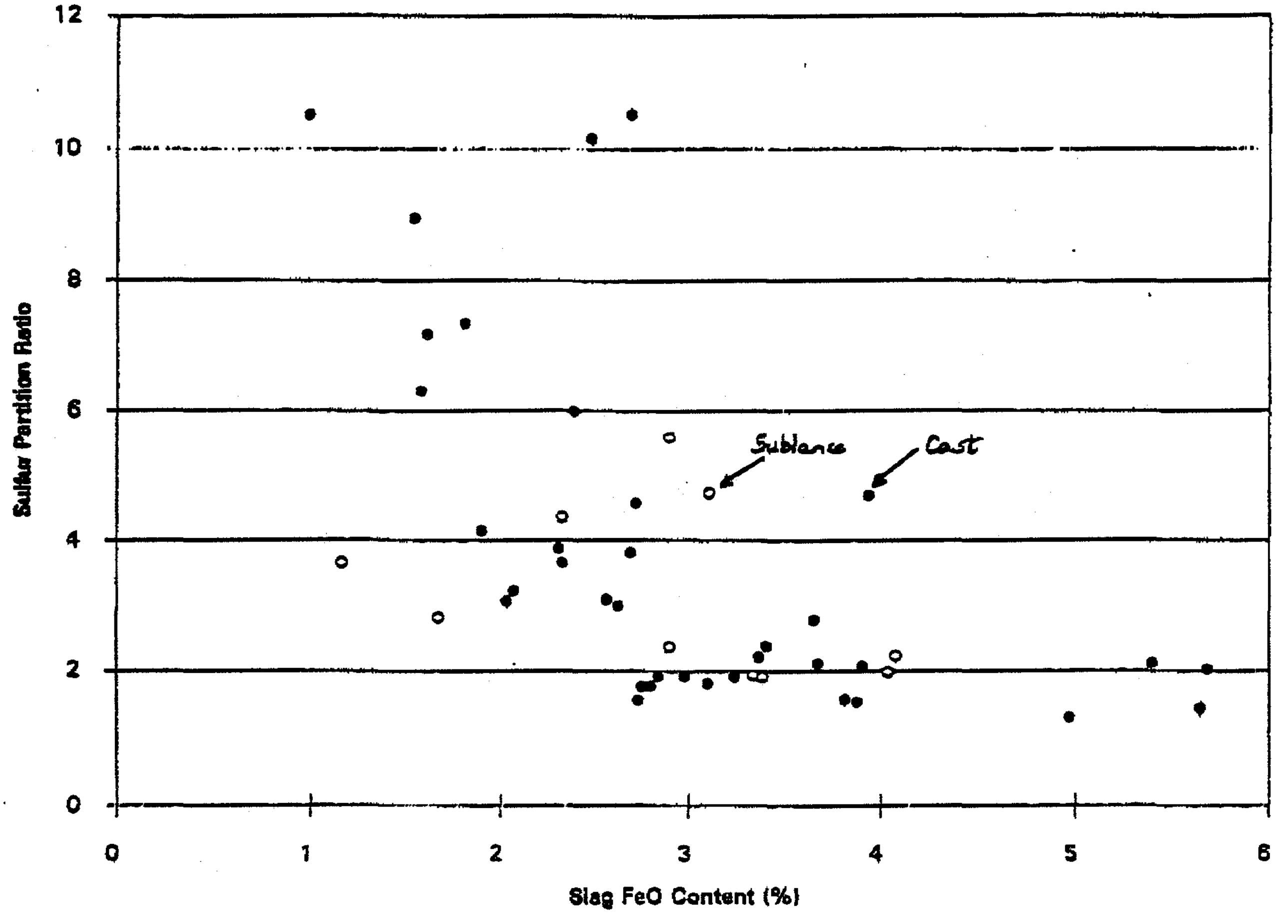
The hot metal sulfur content is mainly dependent on the lime-to-silica ratio in the slag, the FeO content, slag and metal weight, and the hot metal temperature. Figure 19 illustrates the variation in the sulfur partition ratio ($L_S = (\%S)_{slag}/[\%S]_{metal}$) with the lime-to-silica ratio.

Figure 19 – Variation in the Sulfur Partition Ratio With the Slag Lime-to-Silica Ratio



These results are similar to those obtained with the vertical and horizontal vessels.[1] Figure 20 shows the variation in L_S with the FeO content of the slag.

Figure 20 – Variation in the Sulfur Partition Ratio with the Slag FeO Content



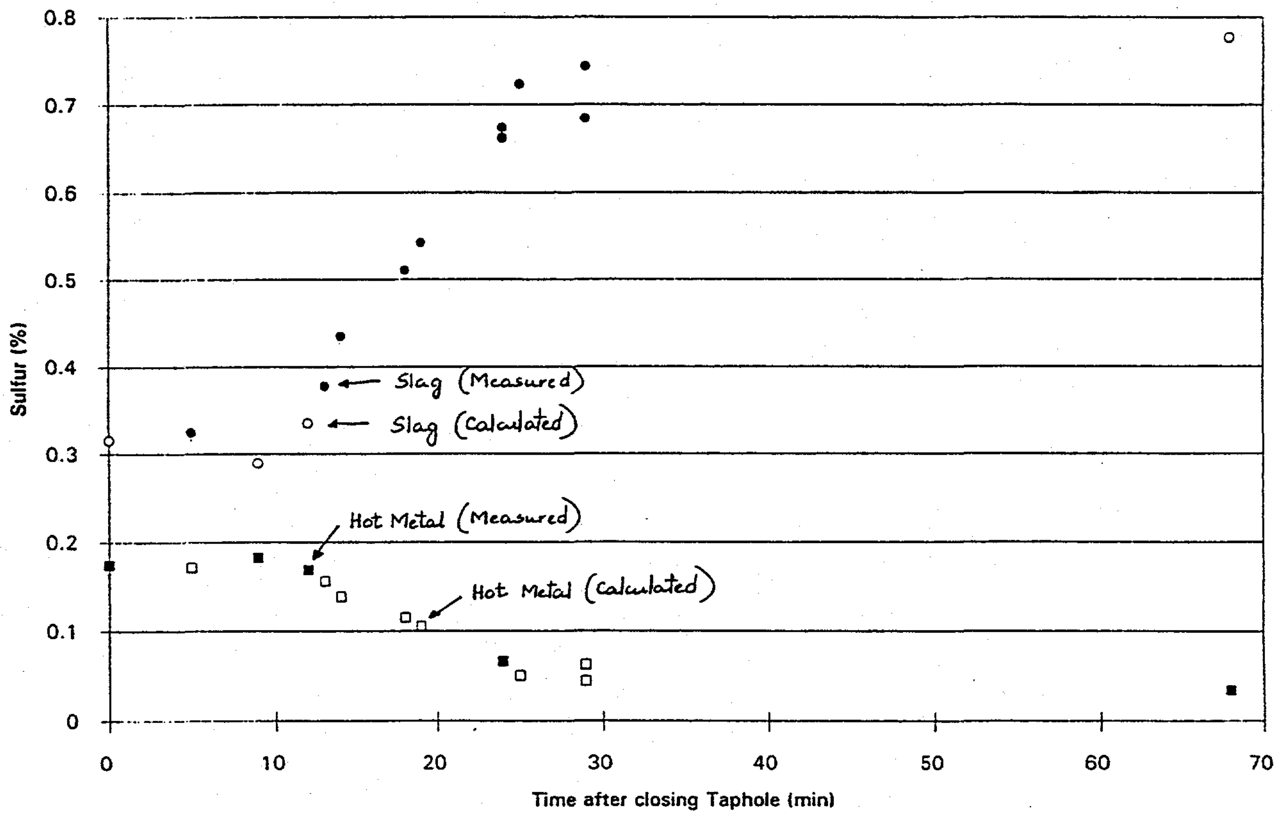
The sulfur content of the hot metal in the DIOS and AISI direct ironmaking situations is in the 0.25 - 0.3% range. In these cases, most of the input sulfur reports to the hot metal and slag due to the presence of a prereducer that acts as a "sulfur trap." Most of the sulfur in the gas and dust entering the prereducer returns to the smelter. Since the only sulfur outlets are the sludge, stack gas, and hot metal/slag, the resultant hot metal sulfur is high.

In the waste oxide recycling situation, the prereducer is eliminated. Consequently, a major portion of the sulfur reports to the sludge. This reduces the amount of sulfur present in the metal and slag. Further, the lime-to-silica ratio in the recycling situation is higher than in the direct ironmaking case due to the raw material composition. Since the sulfur partition is directly related to the lime-to-silica ratio in the slag, the hot metal sulfur content would be further lowered.

In conclusion, it can be said that, based on the pilot plant results, the sulfur path during smelting of waste oxides has been characterized. For given operating conditions, the sulfur distribution can be quantified, and the hot metal sulfur content can be estimated.

Hot Metal Sulfur After Ladle Treatment. A technology for desulfurization of the tapped hot metal from the smelter was developed at the pilot plant. The hot metal sulfur content was lowered to the level present in the blast furnace hot metal by slag-metal mixing, reducing the FeO content of the slag, and using the desulfurization capacity of the slag. The sulfur content of the metal and slag during a desulfurization test is shown in Figure 21.

**Figure 21 – Sulfur Content of Metal and Slag
During the Ladle Desulfurization Test (Trial R14)**



The postsmelting hot metal desulfurization experiments demonstrated proof of concept, and an invention disclosure is being filed. The objective of the tests was to show the desulfurization potential of the smelter slag. The results showed that the smelter slag is far from saturated in sulfur and that the slag FeO and hot metal sulfur could be substantially reduced. This simple ladle treatment leads to increased Fe yield and hot metal desulfurization levels comparable to standard blast furnace practices.

Alkali and Halide Management

Mass balances for alkalis and halogens are shown in Tables 8 through 11. The data presented here are for the instances where samples of water and dust/sludge were taken simultaneously. The amount of alkali metals and halogens calculated in the cyclone dust/sludge/water exceeded that estimated to be in the input materials. The discrepancy in mass balance closure is most likely due to inaccurate chemical analysis. Therefore, the distribution of these species was examined, based on their measured outputs.

For potassium, it can be seen that 70 - 90% of the output was present in the contact water. The balance was distributed almost equally between the cyclone dust and sludge. In the case of sodium, again, 50 - 90% of the output was in the contact water. However, the ratio of the amount of sodium present in the smelter sludge to that in the cyclone dust was greater than 8:1. This implies that sodium that did not report to the contact water and was present mainly in the sludge.

For chlorine and fluorine, more than 95% of the output was present in the contact water. The chlorine and fluorine content of the cyclone dust for Trial R13 showed that the amounts of chlorine and fluorine present were less than 0.1 kg/h and 0.2 kg/h, respectively. This was less than 1% of the output. Thus, for both chlorine and fluorine, more than 95% of the output was present in the contact water, while the cyclone dust contained less than 1%.

The pilot plant results can be summarized as follows. About 70 - 90% of the sodium and potassium was present in the contact water. For chlorine and fluorine, more than 95% was present in the contact water.

Tables 8 and 9

Table 8 : Recycle Trials - Mass Balances for Potassium

Trial #	Time	K2O (In) (kg/h)	K2O (CD) (kg/h)	K2O (SS) (kg/h)	K2O (Water) (kg/h)	In-Out (kg/h)	Closure (%)	CD/In (%)	SS/In (%)	Water/In (%)	Out (kg/h)	CD/Out (%)	SS/Out (%)	Water/Out (%)
9	18:00	61.62	4.96	0.36	47.43	8.87	85.61	8.05	0.58	76.97	52.75	9.40	0.68	89.91
10	12:30	12.57	0.96	3.01	1.48	7.12	43.36	7.64	23.95	11.77	5.45	17.61	55.23	27.16
10	14:00	42.48	3.63	1.91	47.43	-10.49	124.69	8.55	4.50	111.65	52.97	6.85	3.61	89.54
11	11:00	12.35	0.01	8.69	2.96	0.69	84.41	0.08	70.36	23.97	11.66	0.09	74.53	25.39
11	21:00	16.13	6.11	2.12	19.27	-11.37	170.49	37.88	13.14	119.47	27.50	22.22	7.71	70.07
12	17:00	16.97	3.02	3.56	44.47	-34.08	300.82	17.80	20.98	262.05	51.05	5.92	6.97	87.11
13	10:30	12.58	4.12	3.74	8.89	-4.17	133.15	32.75	29.73	70.67	16.75	24.60	22.33	53.07
13	13:30	12.93	5.99	2.28	23.72	-19.06	247.41	46.33	17.63	183.45	31.99	18.72	7.13	74.15
13	16:30	15.90	4.98	8.03	34.09	-31.20	296.23	31.32	50.50	214.40	47.10	10.57	17.05	72.38
13	19:30	10.83	3.44	3.64	56.33	-52.58	585.50	31.76	33.61	520.13	63.41	5.43	5.74	88.83
14	15:00	24.78	1.96	3.01	40.02	-20.21	181.56	7.91	12.15	161.50	44.99	4.36	6.69	88.95
14	17:00	20.83	2.43	3.29	29.65	-14.54	169.80	11.67	15.79	142.34	35.37	6.87	9.30	83.83
14	19:00	9.49	0.59	1.59	11.86	-4.55	147.95	6.22	16.75	124.97	14.04	4.20	11.32	84.47
14	20:00	10.64	5.52	3.65	23.72	-22.25	309.12	51.88	34.30	222.93	32.89	16.78	11.10	72.12

Table 9 : Recycle Trials - Mass Balances for Sodium

Trial #	Time	Na2O (In) (kg/h)	Na2O (CD) (kg/h)	Na2O (SS) (kg/h)	Na2O (Water) (kg/h)	In-Out (kg/h)	Closure (%)	CD/In (%)	SS/In (%)	Water/In (%)	Out (kg/h)	CD/Out (%)	SS/Out (%)	Water/Out (%)
9	18:00	9.46	0.78	0.16	-6.63	15.15	-60.15	8.25	1.69	-70.08	-5.69	-13.71	-2.81	116.52
10	12:30	3.66	0.04	0.29	-3.32	6.65	-81.69	1.09	7.92	-90.71	-2.99	-1.34	-9.70	111.04
10	14:00	11.09	0.39	2.98	9.95	-2.23	120.11	3.52	26.87	89.72	13.32	2.93	22.37	74.70
11	11:00	3.50	0.07	0.82	-9.95	12.56	-258.86	2.00	23.43	-284.29	-9.06	-0.77	-9.05	109.82
11	21:00	11.34	0.95	6.66	4.97	-1.24	110.93	8.38	58.73	43.83	12.58	7.55	52.94	39.51
12	17:00	9.74	0.50	3.56	21.55	-15.87	262.94	5.13	36.55	221.25	25.61	1.95	13.90	84.15
13	10:30	4.07	0.08	0.49	4.97	-1.47	136.07	1.92	12.04	122.11	5.54	1.41	8.85	89.74
13	13:30	17.58	0.78	6.34	9.95	0.51	97.10	4.44	36.06	56.60	17.07	4.57	37.14	58.29
13	16:30	33.87	1.16	12.64	14.92	5.15	84.79	3.42	37.32	44.05	28.72	4.04	44.01	51.95
13	19:30	3.14	1.69	6.44	11.60	-16.59	628.34	53.82	205.10	369.43	19.73	8.57	32.64	58.79
14	15:00	14.15	0.45	13.09	29.84	-29.23	306.57	3.18	92.51	210.88	43.38	1.04	30.18	68.79
14	17:00	11.61	0.55	10.49	11.60	-11.03	195.00	4.74	90.35	99.91	22.64	2.43	46.33	51.24
14	19:00	2.74	0.15	3.29	8.29	-8.99	428.10	5.47	120.07	302.55	11.73	1.28	28.05	70.67
14	20:00	3.08	1.40	6.46	19.89	-24.67	900.97	45.45	209.74	645.78	27.75	5.05	23.28	71.68

In stands for the total input, CD stands for cyclone dust, SS represents the smelter sludge, Water indicates the amount reporting to the contact water system, and Out represents the sum of the cyclone dust/smelter sludge/water. Closure is defined as the percentage of the input present in the CD/SS/Water.

Tables 10 and 11

Table 10 : Recycle Trials - Mass Balances for Chlorine

Trial #	Time	Cl (In) (kg/h)	Cl (CD) (kg/h)	Cl (SS) (kg/h)	Cl (Water) (kg/h)	In-Out (kg/h)	Closure (%)	CD/In (%)	SS/In (%)	Water/In (%)	Out (kg/h)	CD/Out (%)	SS/Out (%)	Water/Out (%)
9	10:00	14.72	0.69	0.08	28.93	-14.98	201.77	4.69	0.54	196.54	29.70	2.32	0.27	97.41
10	12:30	6.63	0.01	0.05	53.41	-46.84	806.49	0.15	0.75	805.58	53.47	0.02	0.09	99.89
10	14:00	21.35	0.16	0.43	31.77	-11.01	151.57	0.75	2.01	148.81	32.36	0.49	1.33	98.18
13	10:30	6.69		0.07	-0.17	6.79	-1.49		1.05	-2.54	-0.10	0.00	-70.00	170.00
13	13:30	10.49		0.40	19.17	-9.08	186.56		3.81	182.75	19.57	0.00	2.04	97.96
13	16:30	17.61		2.21	30.17	-14.77	183.87		12.55	171.32	32.38	0.00	6.83	93.17
13	19:30	5.50		0.53	14.28	-9.31	269.27		9.64	259.64	14.81	0.00	3.58	96.42
14	15:00	14.67		0.46	21.27	-7.06	148.13		3.14	144.99	21.73	0.00	2.12	97.88
14	17:00	12.24		0.44	32.25	-20.45	267.08		3.59	263.48	32.69	0.00	1.35	98.65
14	19:00	4.57		0.23	22.00	-17.66	486.43		5.03	481.40	22.23	0.00	1.03	98.97
14	20:00	5.24		0.24	18.75	-13.75	362.40		4.58	357.82	18.99	0.00	1.26	98.74

Table 11 : Recycle Trials - Mass Balances for Fluorine

Trial #	Time	F (In) (kg/h)	F (CD) (kg/h)	F (SS) (kg/h)	F (Water) (kg/h)	In-Out (kg/h)	Closure (%)	CD/In (%)	SS/In (%)	Water/In (%)	Out (kg/h)	CD/Out (%)	SS/Out (%)	Water/Out (%)
9	10:00	13.91	0.61	1.06	15.04	-2.80	120.13	4.39	7.62	108.12	16.71	3.65	6.34	90.01
10	12:30	0.97	0.01	0.52	2.24	-1.80	285.57	1.03	53.61	230.93	2.77	0.36	18.77	80.87
10	14:00	13.47	0.15	1.29	9.70	2.33	82.70	1.11	9.58	72.01	11.14	1.35	11.58	87.07
13	10:30	0.85		0.40	-1.18	1.63	-91.76		47.06	-138.82	-0.78	0.00	-51.28	151.28
13	13:30	2.80		0.47	11.33	-9.00	421.43		16.79	404.64	11.80	0.00	3.98	96.02
13	16:30	5.61		1.28	38.77	-34.44	713.90		22.82	691.09	40.05	0.00	3.20	96.80
13	19:30	0.76		0.34	24.14	-23.72	3221.05		44.74	3176.32	24.48	0.00	1.39	98.61
14	15:00	7.82		0.34	8.92	-1.44	118.41		4.35	114.07	9.26	0.00	3.67	96.33
14	17:00	6.32		0.70	22.49	-16.87	366.93		11.08	355.85	23.19	0.00	3.02	96.98
14	19:00	0.58		0.24	11.70	-11.36	2058.62		41.38	2017.24	11.94	0.00	2.01	97.99
14	20:00	0.69		0.51	15.17	-14.99	2272.46		73.91	2198.55	15.68	0.00	3.25	96.75

In stands for the total input, CD stands for cyclone dust, SS represents the smelter sludge, Water indicates the amount reporting to the contact water system, and Out represents the sum of the cyclone dust/smelter sludge/water. Closure is defined as the percentage of the input present in the CD/SS/Water.

Neural Network Modeling by Praxair

Under a research contract with this program, Praxair developed a neural net to predict the degree of postcombustion (PCD) as a function of 17 selected inputs, including material feed rates, slag composition, metal and slag weights, lance position, and other process variables on which data were available.

Results show that the nets could predict very well the **test** data from the trials on which they were trained but were unable to predict a new trial on which they were not trained. This may be attributed to less than required variability in the training data and that five of the inputs were calculated and/or interpolated values.

At the current stage, the application of neural networks is NOT recommended for the AISI waste oxide recycling process, based on the results obtained in this study. However, when the demonstration plant is running and more operating data become available, neural networks will be a good tool to provide further information about process optimization and control.

Refractory Performance

Because severe refractory wear was experienced in the postcombustion slag zone of the smelter, the smelter vessel design was provided with stave cooling to retard lining wear, and additional staves were added during the program. The stave and refractory system was designed to provide a frozen slag layer on the inner face of a stable brick lining under controlled conditions of slag composition and temperature. An invention disclosure has been submitted on this design which consists of special water-cooled copper staves and a combination of refractories, carefully selected for their heat transfer properties, supporting the frozen slag layer. The formation of a stable brick thickness would provide improved lining life at reasonable levels of heat loss. The actual stable thicknesses measured in the various areas of the vessel are shown in Table 12. The refractory profile after a waste oxide recycling campaign was illustrated in Figure 8, page 22.

Table 12 – Comparison of Stable Thickness in Smelter Lining

Area	Construction	Stable Refractory Thickness, mm
Cone	Gun / cooled	25 - 30
Upper barrel	Brick / cooled	150 - 175
Mid barrel	Brick / cooled	0 - 100
Lower barrel / bottom	Brick - ins	None

As can be seen from Table 12 and Figure 8, the refractory was worn back to the copper panels in a narrow band in the vicinity of the upper slag. Based on the results of the direct ironmaking and waste oxide recycling trials, the following comments and recommendations were offered.

The overall lining performance of the smelter will be improved. Some of this improvement will undoubtedly result from long-term operation under stabilized conditions and the avoidance of the thermal cycling as in the pilot plant. Significant further improvements are also expected to result from the following proposed design criteria.

The staves for the brick/cooled zone will be located as near as possible to the metal/collapsed slag zone, i.e., somewhat lower in the vessel than the current lining. The coolers will all be installed with the copper "c" cups now used in the gun-cooled zone to allow slag buildup in the event that the refractory is completely worn. The staves will also be designed in a manner to provide sectional refractory support if the underlying refractory is worn.

The alumina-chromic oxide brick safety lining in the brick/insulated zone will be used for at least one foot below the staves. The taphole area will follow the design (carbon block, etc.) successfully used in modern blast-furnace construction.

The use of a combined design using gun-cooled areas, brick-cooled areas, and brick-insulated areas should prove successful with reasonable levels of heat loss.

Composition and Properties of Hot Metal and Slag

Samples of the slag and metal from the vessel were obtained using the sublance. Samples of slag and metal were also taken from the casting boxes. Tables 13 and 14 show the hot metal and slag composition for Trial R12.

The hot metal was carbon-saturated and contained more than 4.5% carbon in all cases. The sulfur level varied between 0.038 - 0.171%. However, in Trials R13 and R14, due to the high-sulfur-containing agglomerate, the hot metal sulfur at cast was as much as 0.3%. The silicon and aluminum levels in the smelter hot metal are very low. In Table 14, aluminum is shown to be present in the hot metal. This is because the samplers used contained aluminum as a deoxidant. In some instances, samplers with zirconium deoxidant were used, and these samples revealed very low aluminum contents. The manganese content of the hot metal was less than 0.3% in most instances while the maximum phosphorus content was 0.08%. Most of the analyses were in the range of 0.03%.

Table 13

Table 13 : Sublance and Cast Slag Chemical Composition (Trial R12)

Sublance Slag Chemical Composition

SAMPLE #	SAMPLE LOCATION	TRIAL #	SAMPLE TIME	ANALYZED BY	LIME RATIO	MgO %	Al2O3 %	MnO %	FeO %	P2O5 %	SiO2 %	Leco C %	Leco S %
1	sublance	R12	1136	AISI	1.26	15.23	9.49	4.32	5.90	0.25	27.49	0.67	0.304
2	sublance	R12	1200	AISI	1.28	16.47	9.67	4.28	5.23	0.23	27.39	0.28	0.277
3	sublance	R12	1221	AISI	1.20	18.16	9.78	3.98	3.85	0.27	28.28	0.40	0.290
4	sublance	R12	1245	AISI	1.10	18.84	10.01	3.32	2.90	0.24	29.77	0.60	0.313
5	sublance	R12	1300	AISI	1.20	18.23	9.23	3.69	4.04	0.25	28.29	0.60	0.290
6	sublance	R12	1410	AISI	0.98	20.60	9.23	2.01	4.08	0.14	31.20	0.64	0.337
7	sublance	R12	1440	AISI	1.05	21.07	9.29	2.13	3.39	0.18	29.99	0.74	0.292
8	sublance	R12	1505	AISI	1.08	21.61	9.14	1.97	3.37	0.14	29.63	0.81	0.311
9	sublance	R12	1640	AISI	1.25	23.60	7.79	1.44	5.28	0.17	26.51	0.34	0.383
10	sublance	R12	1715	AISI	1.30	21.65	7.93	1.53	4.31	0.20	27.04	0.41	0.413
11	sublance	R12	1730	AISI	1.22	23.45	8.07	1.31	3.66	0.18	27.51	0.40	0.437
12	sublance	R12	1915	AISI	1.26	22.12	8.04	1.46	3.94	0.21	27.40	0.35	0.375
13	sublance	R12	1943	AISI	1.29	21.52	7.96	1.58	3.68	0.22	27.47	0.32	0.330
14	sublance	R12	2005	AISI	1.26	23.39	7.78	1.48	4.83	0.26	26.74	0.21	0.303
15	sublance	R12	2020	AISI	1.26	22.39	8.10	1.49	4.23	0.24	27.24	0.29	0.277
16	sublance	R12	2050	AISI	1.23	22.54	8.22	1.43	2.82	0.24	28.18	0.39	0.258
17	sublance	R12	2110	AISI	1.29	21.36	8.08	1.54	2.68	0.19	28.02	0.38	0.231
18	sublance	R12	2140	AISI	1.27	18.32	8.20	1.61	2.48	0.19	28.72	1.83	0.207
19	sublance	R12	2143	AISI	1.34	20.06	8.11	1.62	2.33	0.19	28.01	0.45	0.209
20	sublance	R12	2210	AISI	1.19	21.88	8.60	1.31	2.03	0.19	29.24	0.54	0.155
21	sublance	R12	2230	AISI	1.29	20.34	8.21	1.57	2.43	0.19	28.53	0.57	0.138
22	sublance	R12	2245	AISI	1.29	19.86	8.26	1.52	2.66	0.19	28.84	0.32	0.140
23	sublance	R12	2110	UEC	1.28	19.55	9.26	1.51	3.18	0.20	28.20	0.47	0.205
24	sublance	R12	2310	UEC	1.28	19.53	10.13	1.47	2.49	0.19	27.67	0.852	0.14

Cast Slag Chemical Composition

SAMPLE #	SAMPLE LOCATION	TRIAL #	Cast #	ANALYZED BY	LIME RATIO	MgO %	Al2O3 %	MnO %	FeO %	P2O5 %	SiO2 %	Leco C %	Leco S %
1	Runner	R12	1	AISI	1.04	19.72	9.64	2.85	2.80	0.24	30.55	0.81	0.270
2	Runner	R12	2	AISI	1.07	22.77	9.35	1.89	2.98	0.15	29.61	0.12	0.272
3	Runner	R12	3	AISI	1.23	25.02	7.67	1.53	2.56	0.18	27.48	0.14	0.393
4	Runner	R12	4	AISI	1.16	26.22	8.03	1.31	2.03	0.23	28.00	0.10	0.312
5	Runner	R12	5	AISI	1.12	30.18	7.45	1.27	1.81	0.21	27.10	0.24	0.279
6	Ladle	R12	Drain	AISI	1.67	10.61	14.36	0.53	38.14	0.15	12.99	0.17	0.170
7	Slag Box	R12	Drain	AISI	1.21	20.66	8.74	1.36	1.75	0.20	29.50	0.77	0.138
8	Runner	R12	5	UEC	1.30	28.50	9.00	1.43	1.48	0.20	24.66	0.23	0.243

Table 14

Table 14 : Sublance and Cast Hot Metal Chemical Composition (Trial R12)

Cast Hot Metal Chemical Composition

SAMPLE #	SAMPLE LOCATION	TRIAL #	Cast #	SAMPLE TIME	ANALYZED BY	Leco C %	Leco S %	Si %	Al %	Mn %	P %	Fe %	Cu %
1	Slug Box	R12	1	1336	AISI	4.72	0.16	0.01	0.11	0.12	0.02	94.14	0.02
2	Slug Box	R12	2	1540	AISI	4.75	0.14	0.01	0.26	0.11	0.03	93.98	0.02
3	Slug Box	R12	3	1803	AISI	4.87	0.13	0.01	0.18	0.12	0.03	93.96	0.01
4	Slug Box	R12	4	1954	AISI	4.91	0.10	0.01	0.18	0.14	0.03	94.00	0.02
5	Slug Box	R12	5	2200	AISI	4.88	0.04	0.03	0.42	0.21	0.06	93.79	0.01
6	Lad Tst	R12	Drain	2340	AISI	4.80	0.06	0.02	0.33	0.16	0.04	94.05	0.01
7	Slag Box	R12	Drain	0025	AISI	4.78	0.04	0.16	0.43	0.12	0.03	93.90	0.01
8	Ind Fce	R12	Ind Fce	700	AISI	4.59	0.09	0.04	0.50	1.12	0.03	92.98	0.02
9	HM Ladle	R12	IF Tap	855	AISI	4.36	0.08	0.01	0.60	1.13	0.03	93.27	0.02
10	Slug Box	R12	4	1954	UEC	4.7	0.098	<.01	0.17	0.13	0.03		0.013
11	Slug Box	R12	5	2200	UEC	4.89	0.039	0.015	0.19	0.23	0.064		0.013

Sublance Hot Metal Chemical Composition

SAMPLE #	SAMPLE LOCATION	TRIAL #	SAMPLE TIME	ANALYZED BY	Leco c %	Leco S %	Si %	Al %	Mn %	P %	Fe %	Cu %
1	sublance	R12	1245	AISI	4.72	0.13	0.08	0.33	0.13	0.02	93.86	0.018
2	sublance	R12	1300	AISI	4.46	0.147	0.15	0.36	0.11	0.02	93.75	0.021
3	sublance	R12	1440	AISI	4.62	0.15	0.15	0.33	0.12	0.02	94.01	0.014
4	sublance	R12	2143	AISI	4.86	0.08	0.05	0.22	0.22	0.08	93.60	0.016
5	sublance	R12	2143	UEC	4.77	0.04	<.01	0.28	0.22	0.083		0.018

During the waste oxide recycling trials, the lime-to-silica ratio in the slag varied depending on whether waste oxides were charged to the smelter. The lime-to-silica ratio during operation with hematite pellets alone was varied between 1 - 1.3. Operation with waste oxides resulted in this ratio being as high as 1.6. The alumina content of the vessel slag was less than 10% in almost all cases. The MgO content of the vessel slag varied between 15 - 23%. The FeO level of the slag was maintained below 6%. The MnO content of the slag when operating with waste oxides was about 1.5%, while the P_2O_5 content was about 0.4%.

Samples of slag from the waste oxide recycling trials were tested for suitability for use in construction applications. These tests indicated that the slag is acceptable with respect to resistance to degradation in handling and freeze-thaw conditions but is marginal in expansion (hydration) under a longtime water soak. This high expansion is related to the high MgO content of the slag. The phenomenon of the formation of yellow (sulfur) type appearance associated with blast-furnace slags under conditions of storage in sealed water jars did not occur with smelter slag used in the ladle desulfurization test.

To make the slag fully acceptable as a construction-type material, the MgO content of the slag must be reduced. This goal is compatible with the concept of a water-cooled stable lining for adequate refractory life. Successful use of the water-cooled lining would reduce the slag MgO content to about 8 - 12% and eliminate the hydration and expansion concerns.

The zinc oxide content of the slag was less than 0.1% in most cases. At a slag production rate of 3.5 tph, this would correspond to 3.5 kg/h of zinc oxide being retained in the slag. The zinc content in the cast metal was less than 0.01% in most cases. At a hot metal production rate of 5 tph, this would correspond to 0.5 kg/h. Thus, the amount of zinc retained in the slag and metal is very small when compared to the input zinc levels. Furthermore, a special blowing and material feeding practice was developed for removal of zinc from the condensed phases. This becomes particularly important with high zinc loads in case of smelting of EAF dust.

The lead oxide content of the slag was always less than 0.1%. The lead content of the metal was less than 0.005% (50 ppm) in all cases except one. The potassium oxide content of the slag was less than 0.05% in all samples except one. The concentration of sodium oxide in the slag was higher than that of potassium oxide and was always less than 0.15%. The chlorine content of the slag was less than 0.01%, while the fluorine content was less than 0.05%. The chlorine content of the metal was 0.004%. The amount of halides and alkalis retained in the slag and metal was small.

Samples of the hot metal and slag produced were analyzed for RCRA (Resource Conservation and Recovery Act) metals, and a TCLP (Toxicity Characteristic Leaching Procedure) was also performed. It was concluded that the hot metal and slag produced during the waste oxide recycling trials did not pose any environmental concern.

KEY FINDINGS AND CONCLUSIONS DRAWN FROM THE PILOT PLANT PROGRAM

A new process to handle steel plant waste oxides was developed at the AISI Pilot Plant using existing technology and equipment. It is now possible to implement an environmentally correct solution to the waste oxide disposal problem at a profit. All types of waste oxides were successfully processed and melted to hot metal in the pilot plant, on time and on budget, to make a success of the Waste Oxide Recycling Program.

Several key factors led to the success of the program. One of the most important was the dedication of the pilot plant staff and crew, acting as a team. The waste recycling pilot plant program began with the first trial on April 28, 1994, and concluded successfully, fourteen trials later, on December 20, 1994. During this time, the staff and crew lived with the process, identified each problem, and worked on it until it was solved. From pretrial setup through verifying instrument and control systems, managing material handling problems and logistics, conducting the trials and gathering data, cleaning up, solving the problems of the trial, and preparing for the next one, this team carried on, each person contributing his energy and expertise where needed.

Without this type of sustained, dedicated effort, the work would not have been completed within the time and funding available. Safety and quality were a way of life. The staff and crew operated a pilot plant with all the problems of a full-scale plant and obtained research-laboratory-quality data and results. This type of effort and expertise was not only demonstrated for the recycling program but also for the 90 trials and five years of the Direct Steelmaking Program.

The second key factor was the solid background in smelter operations that was gained during the Direct Steelmaking Program. During the Waste Recycling Program, it was unnecessary to devote time and resources to learning and commissioning new systems. Very few equipment changes were made to the operating equipment for the Recycling Program; most vessel equipment systems had already been modified and were operational. Of great importance was that the design and operation of the oxygen lance were established during the Direct Steelmaking Program, and only small refinements were needed during the Recycling Program.

The time and experience gained during the Steelmaking Program also established a firm foundation for the smelter control systems and data acquisition system. There was a solid system in place, and only refinements and incremental improvements were required. Most changes were made to improve system reliability and usefulness to the operator with the goal that operators, rather than engineers, would be able to run the process.

The offgas sampling system, a key input device for the process control system developed by the AISI staff and used during the Direct Steelmaking Program, was continually improved during that program. The high degree of confidence in the system fostered a high level of confidence in the operation and control of the plant when processing the waste oxides. Improvements to the material feed system to better control the discharge rate of material into the vessel improved the process stability and increased the reliability of the on-line mass and energy balances. The results of the balances were monitored and were used by the operators to control the process.

One factor in the success of the program was the stable nature of the process itself over a wide range of operating conditions and raw materials. Excursions could be studied to optimize the process, with the confidence that there were extremely stable conditions or ranges to which the operators could return if a problem arose. In case of an upset, the process responded quickly to corrective actions, and total recovery, the return to aim hot metal temperature and production rates, could be achieved in less than 30 minutes. Not only was the process easy to start up and shut down, but even after a one-to-two-hour shutdown, restart and return to previous conditions could be achieved within 30 to 40 minutes. With the knowledge gained at the pilot plant, modifications to the demonstration plant design will be made to allow for an even easier total startup and shutdown procedure.

Refractory wear was a problem that had long plagued in-bath smelting processes. Knowledge gained regarding water cooling of refractories during work with the horizontal (second) vessel was applied to the third smelter vessel. During the Recycling Program, the level of experience in water-cooled refractories was increased further. The design of a water-cooled refractory system has now been developed to the extent that good refractory wear and long campaign life can be expected for long-term operation without extreme heat losses to the process. This is a milestone achievement in process development.

Also, concerning refractory cost, the casthouse design was modified in the Recycling Program to greatly simplify casting. A simple runner is the only equipment necessary to remove metal and slag from the vessel and into a ladle. The same ladle, equipped with bottom stirring, can be used for desulfurization, followed by either feeding a pig machine or transferring to a torpedo car, and remaining ready for the next cast.

A key factor in process economics has been the hot metal sulfur levels. The use of smelter slag to desulfurize the hot metal outside the vessel, after cast, has resolved that problem with a very simple, low-cost solution. Discovering that the zinc in the offgas captures the sulfur in the gas and transfers it to the sludge, where it is used by the zinc company, completed the solution to the sulfur problem.

With the modifications made to the offgas system, it was possible to operate at and see the effects of higher system pressures. The process was more stable at higher levels of postcombustion with higher pressures. For a recycling plant with no prereduction requirements, the system can tolerate a wide range of temperatures so that no recycling loop is required. This will reduce the cost of a recycling plant. Also, the engineering and operational requirements of the cyclone and offgas duct system for a demonstration plant can now be specified.

The environmental testing completed during the Recycling Program confirmed that air and water standards have been met and that the slag is comparable to blast furnace slag and can be used in the same fashion. The sludge can be used as a feedstock for zinc production. The process is environmentally friendly; waste oxide materials and fuel come to the site, and only products come out. The environmental problems have been solved, not merely reduced or relocated.

FEASIBILITY STUDY

PROCESS FUNDAMENTALS

A comprehensive experimental program was conducted by the AISI-DOE Direct Steelmaking and Waste Oxide Recycling Programs to study the fundamentals of the smelting process. Laboratory-scale investigations were carried out at Carnegie Mellon University, Massachusetts Institute of Technology, McGill University, McMaster University, and the research laboratories of Praxair and U. S. Steel. The pilot plant tests were conducted at Universal, Pennsylvania, at a facility leased from United States Steel. The results of the laboratory and pilot plant investigations have been summarized in annual reports to the DOE.[2] Based on these studies, significant progress has been made in understanding the process fundamentals. A brief review of the technical issues pertinent to the smelting process is presented.

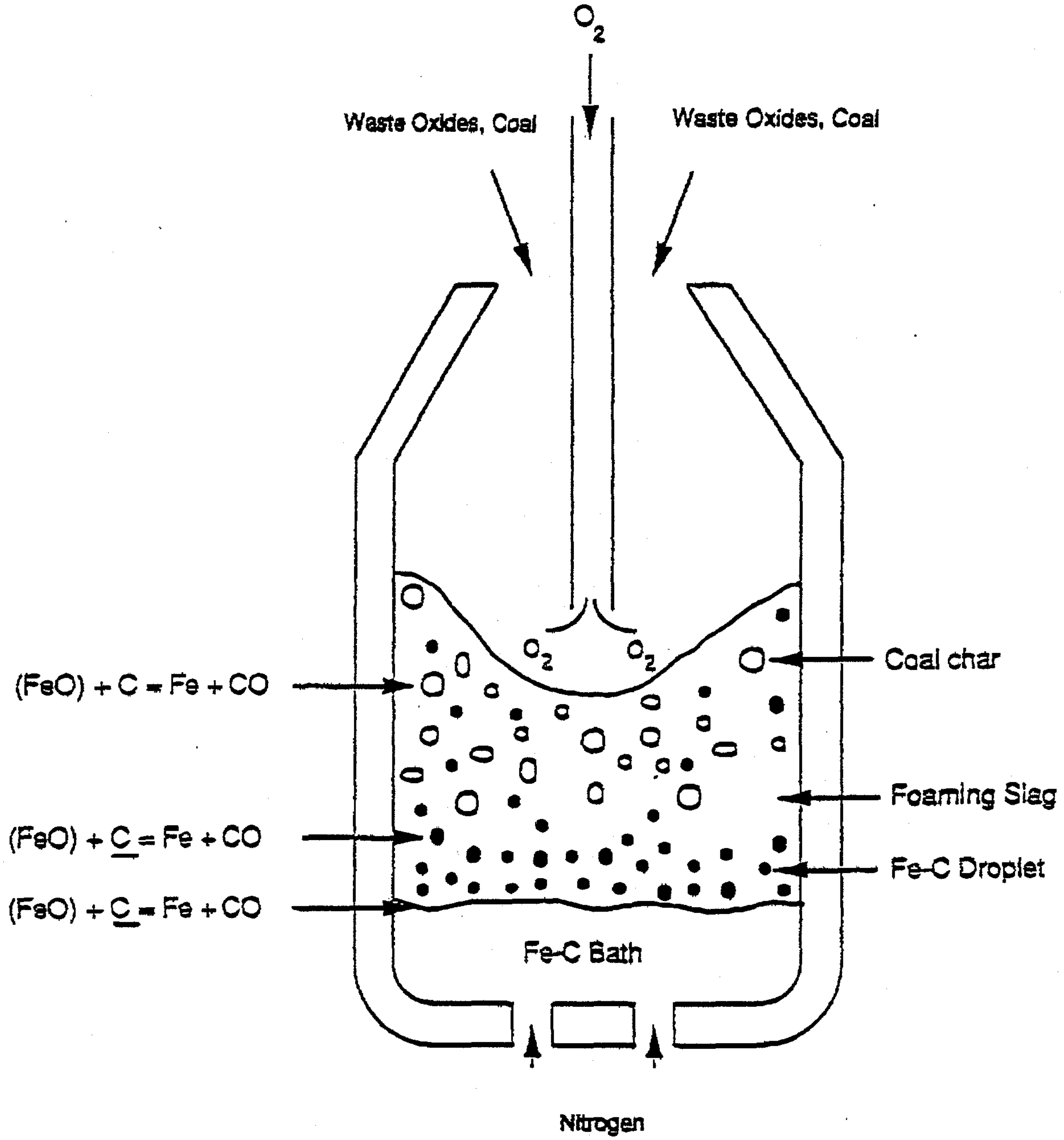
Smelting Reactor Description

Figure 22 shows a schematic of the smelting reactor. The bottom of the reactor contains a molten iron-carbon bath that is stirred by inert gas. Above the iron bath is a slag containing low amounts of FeO (about 5%). The slag consists of a dense slag region and a foamed slag zone. The dense slag region has molten iron droplets dispersed in it. These droplets are present due to emulsification of part of the iron bath caused by the agitation provided by the inert gas. In addition, iron droplets produced by reduction are also present in the dense slag region.

Primary combustion and the reduction of iron oxides result in the evolution of CO gas which causes part of the slag to foam. Some slag is also thrown up into the free space, and these slag particles are referred to as spatter. The slag also contains char that remains after the coal has been devolatilized. The size distribution of the char present in the slag has implications with respect to reduction of iron oxides and slag foaming. Slag foaming is controlled by maintaining a critical char-to-slag ratio.

The slag is crucial to the smelting process since it is the reduction and heat transfer medium and it insulates the metal bath and the refractories from the postcombusted gases and oxygen jets. The distribution of raw materials and oxygen is also an important issue with respect to heat generation and heat transfer.

Figure 22 – Schematic of Smelting Reactor



The key phenomena occurring in the smelting reactor are the dissolution of iron oxides in the slag, devolatilization of coal and dissolution of carbon into iron, reduction of iron oxide from the slag, slag foaming or release of gas from the slag, postcombustion and heat generation, and heat transfer from the combustion reactions to the process. The production capacity of a smelting reactor can be limited by any one or a combination of these subprocesses. The above phenomena were the primary focus of the laboratory investigations and were extensively studied during pilot plant operation. The results of laboratory and pilot plant investigations are summarized in the following sections.

Devolatilization of Coal

The devolatilization of coals under smelting conditions in the gas and slag phases has been studied in detail.[3,4] The rate of devolatilization was found to be independent of the coal type and the medium in which the devolatilization occurred. The amount of volatiles liberated was found to be greater than that estimated by the proximate analysis of the coal. This was attributed to the rapid heating to a higher temperature in the case of smelting conditions as compared to the conditions used in the proximate analysis test. The devolatilization rate was a strong function of the particle size. It was concluded that the devolatilization rate was primarily heat transfer controlled. At the pilot plant, environmental testing of the hydrocarbon content of the offgases, sludge, and contact water was conducted. It was concluded that the level of hydrocarbons present does not present any environmental concern. This is illustrative of an inherent advantage of the AISI-DOE postcombustion smelting technology in which the high temperature causes the rapid breakup of hydrocarbons, allowing the direct use of coals.

Carbon Dissolution into Iron

The rate of dissolution of carbon into iron has been experimentally investigated.[5] The dissolution rates were affected by sulfur in the hot metal and ash in the char. During the pilot plant trials, the hot metal cast was carbon-saturated. This was accomplished by the high degree of stirring prevalent and by maintaining an adequate amount of char in the slag.

Dissolution of Iron Oxides

This was investigated by using hematite and wustite pellets.[6] The pellets were found to dissolve quickly. A heat transfer model developed to estimate dissolution rates showed that the predicted dissolution time was less than five seconds. The amount of undissolved pellets in the slag at any time was estimated to be less than 1%. These results have been confirmed at the pilot plant, in that undissolved pellets or waste oxide briquettes have not been found in the slag samples.

Reduction of Iron Oxides

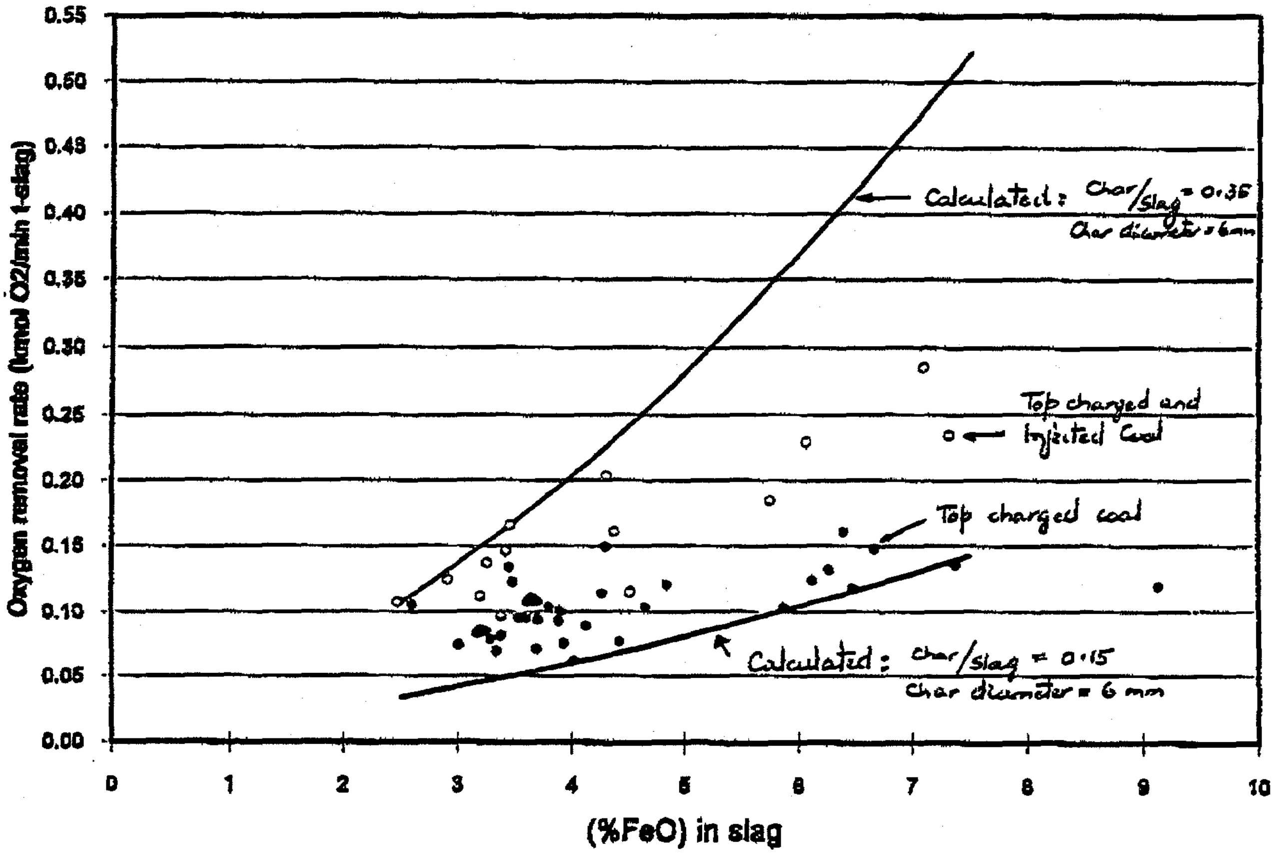
In the smelting reactor, reduction occurs in the liquid phase. Mass transfer processes and chemical kinetics occur more rapidly; consequently, the productivity of the reactor is greater.

The smelting vessel has about three times higher production per unit volume than the blast furnace where reduction mainly takes place in the solid state. Extensive work has been conducted to understand the reduction reactions occurring in the smelting process.[7,8]

The reduction of iron oxide from the slag is done by char, iron-carbon droplets, and the slag-metal interface. The droplets in the slag come from (1) emulsification of part of the iron bath and (2) iron produced by the reduction reactions. The reduction rate by iron-carbon droplets is affected by the carbon and sulfur content of the droplets and is proportional to the FeO content of the slag.[7] The reduction rate by char is primarily controlled by mass transfer of FeO in the slag[8] and is approximately proportional to the FeO content of the slag.

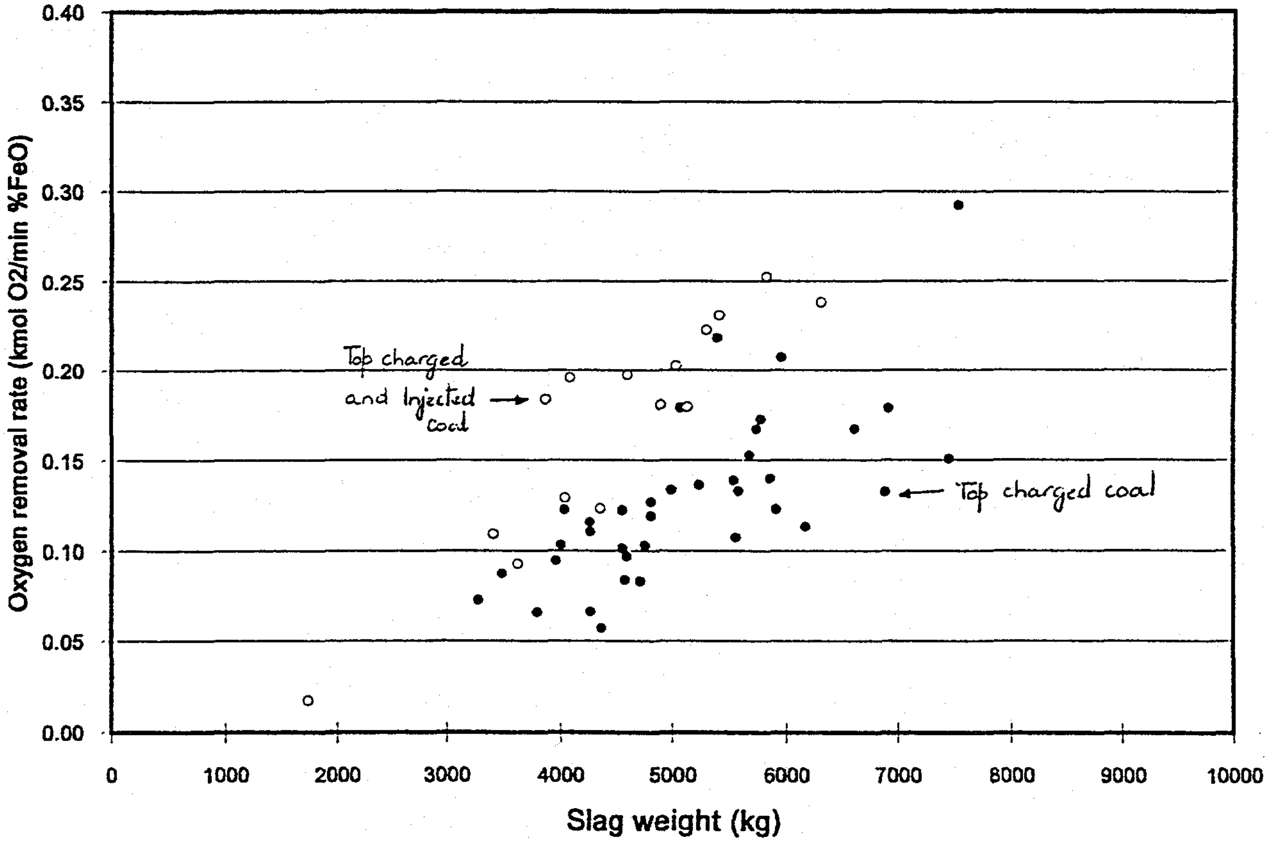
The reduction kinetics govern the relationship between the FeO content of the slag, the char weight and size, slag weight, size and amount of iron-carbon droplets, and the iron oxide charging rate. Figure 23 illustrates the relationship between the above parameters.

Figure 23 – Oxygen Removal Rate Per Unit Slag Weight
As a Function of the Slag FeO Content



Here, the oxygen removal rate per unit slag weight is plotted against the FeO content of the slag. The solid lines represent calculated values based on a reduction model.[8] The oxygen removal rate is representative of the iron oxide charging rate. The following conclusions can be drawn. A higher iron oxide charging rate results in a higher slag FeO, other parameters being constant. The use of coal injection, which results in a smaller char size distribution, reduces the FeO content of the slag. For a given iron oxide charging rate, the slag weight required to maintain a fixed FeO level can be estimated. Figure 24 shows the effect of slag weight on the oxygen removal rate expressed per unit FeO content of the slag. Again, the same conclusions can be drawn.

Figure 24 – Oxygen Removal Rate Per Unit Slag FeO Versus Slag Weight



Slag Foaming

The slag foam is important to the smelting process since it captures the heat from the combustion reactions and it insulates the metal bath and refractories from the offgas and oxygen jets. On the other hand, excessive slag foaming results in operating problems and limits productivity. Slag foaming has been extensively studied in the laboratory[9,10] and at the pilot plant.[1]

Slag foaming is represented by the foam index which is a measure of the travel time of the gas in the slag.[9,10] Laboratory investigations have shown that foaming is directly affected by the slag viscosity and offgas velocity, while it is inversely dependent on the bubble diameter.[11]

At the pilot plant, the slag height was measured by a conductivity probe developed specially for this pilot plant. In earlier trials with the vertical and horizontal vessels, a chain was used to measure the slag and spatter height. The laboratory results on foaming were confirmed at the pilot plant. In addition, the slag height was affected by the char weight, the lance gap, and slag temperature. The size distribution of the char for foam control was also found to be important.

Heat Generation and Heat Transfer

In the smelting reactor, the energy generation and utilization per unit reactor volume is high. The high endothermic requirement created by the rapid reduction reactions is satisfied by a combination of primary and postcombustion. At 40% postcombustion, more than half the energy is supplied by postcombustion. Oxygen and raw material distribution play an important role in heat generation. In addition, operating parameters such as char weight, lance height, and operating pressure also affect heat generation.

The behavior of oxygen jets in a high temperature atmosphere has been experimentally studied.[12] A mathematical model describing the phenomenon and able to estimate the penetration of the oxygen jets and the jet profiles was developed.[13]

The heat from the postcombustion reactions is transferred to the incoming raw material stream, slag spatter in the free space, and char and metal droplets in the strongly-stirred slag. In addition, some heat is radiated to the refractory and water-cooled walls of the vessel and is essentially lost from the process. During the pilot plant trials with waste oxides, about 80 - 85% of the heat generated in the smelting reactor was used for smelting purposes. The remainder was lost to the refractories, water-cooled walls, and as superheat in the offgas. Previous work has shown that heat transfer to the process scales up volumetrically rather than with the cross-sectional area.[1]

Thermodynamics of Na_2O, K_2O, PbO, and ZnO in Slags

The support research to the AISI Waste Oxide Recycling Program at Carnegie Mellon University was concerned with the thermodynamics of dilute components in slags relevant to waste oxides and the kinetics of postsmelting desulfurization.

Dust from the BOF, BF, and EAF contains significant amounts of zinc, lead, and alkalis. It is estimated that most of these elements will enter the gas phase, but some will remain in the slag. To calculate the distribution between the slag and gas phases, the activities in the slag must be known. An extensive literature survey was conducted to determine our current state of knowledge on these activities, and if there was insufficient information, experiments would be conducted. The major findings of the literature review are given below.

1. The activity of Na_2O in slags is well known. Despite large negative deviations from ideal behavior, almost all the Na goes to the gas. It was shown that less than 0.003% Na_2O will remain in the slag at 1500°C, assuming the oxygen potential in the slag is controlled by Fe-FeO equilibrium.

$$\mathrm{Fe} + (\mathrm{Na_2O}) = \mathrm{FeO} + 2\ \mathrm{Na}\ (\mathrm{gas})$$

2. The activity of K_2O in blast furnace slags has been measured. Using this information and a reaction similar to the equation above, it is shown that less than 0.005% K_2O will remain in the slag.

3. The activity of ZnO in slags is not accurately known except that the activity coefficient is greater than unity. Depending on the assumed activity coefficient, the ZnO content would range from less than 0.005 to 0.2% in the slag. Similar behavior for PbO is expected.

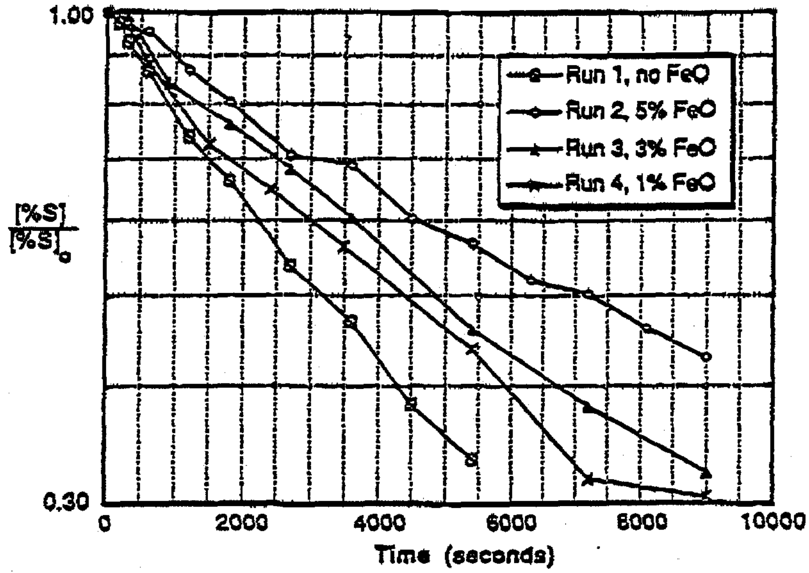
Based on the literature review and extensive thermodynamic calculations, no experimental work was considered necessary.

Hot Metal Desulfurization

Most of the experimental work and mathematical modeling were concerned with desulfurization of the smelter metal. Experiments have been conducted to determine the effects of Si in the metal and FeO in the slag on desulfurization and on the reduction of FeO by carbon after smelting. FeO in the slag reduces desulfurization by decreasing the sulfur distribution ratio. Si increases the rate of FeO reduction and desulfurization. The results are summarized below:

1. In laboratory experiments, FeO reduces the rate of desulfurization as shown in Figure 25.

Figure 25 – Results from Small-scale Experiments - Sulfur in Metal



2. Si in the metal increases the rate of desulfurization.

3. Based on the experimental results, a mathematical model for desulfurization was developed, assuming that the rate is controlled by the transfer of S and "FeO" in the slag and S and Si in the metal. Using this model, the rates of the reduction of FeO and desulfurization were computed for a hypothetical postsmelting desulfurization process in which the smelting slag is used for desulfurization. The main objective was to determine the effect of Si. The calculated sulfur in the metal and FeO in the slag are shown in Figures 26 and 27. The results suggest 0.3% Si in the metal significantly improves desulfurization; more Si is of little benefit. These results encouraged and aided a successful pilot plant trial on postsmelting desulfurization.

Figure 26 – Model Results: Metal Sulfur Content vs. Time

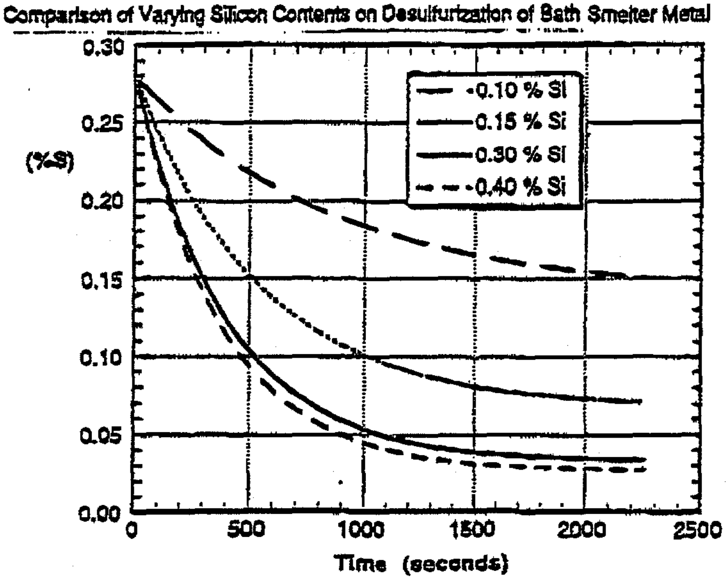
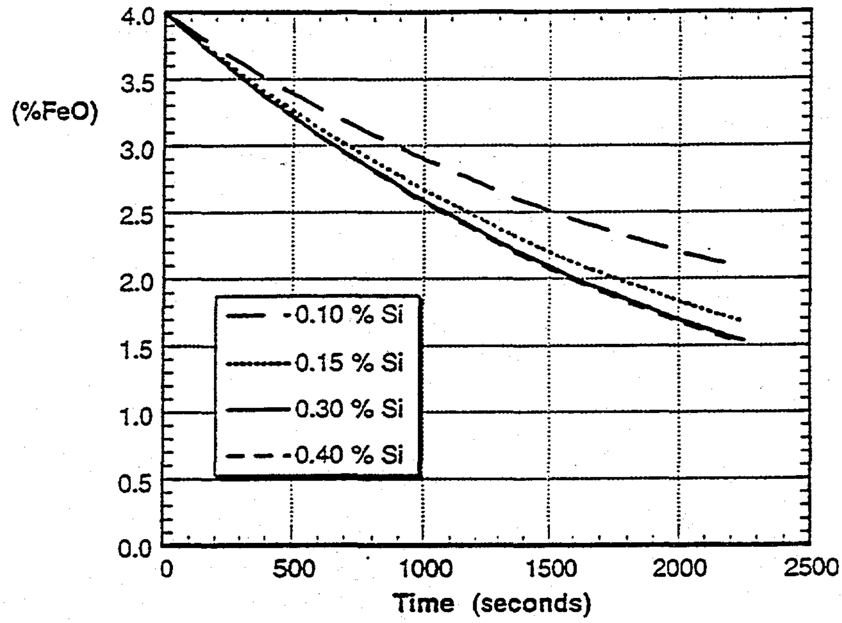


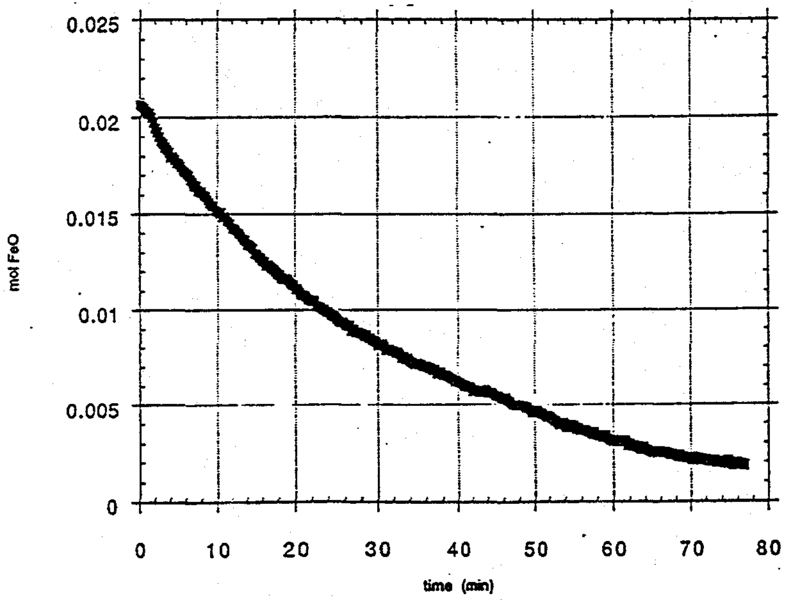
Figure 27 – Model Results: Slag FeO Content vs. Time

Comparison of Varying Silicon Contents on FeO Reduction out of Bath Smelting Slag



4. The rate of reduction of FeO and desulfurization by carbon only after smelting is also being investigated. The rate of reduction of FeO depends on sulfur but not carbon except for its effect on the activity of sulfur. The rate was measured using a constant volume pressure increase (CVPI) technique to measure the rate of evolution of CO. Typical results for the reduction of FeO are shown in Figure 28. Water modeling was carried out to estimate the mass transfer parameters for postdesulfurization with large slag volumes. This work is continuing under the sponsorship of CISR and will be reported to AISI.

Figure 28 – Mole FeO Present vs. Time



SCALEUP CRITERIA AND PROCESS DESIGN

The successful scaleup of a process requires the knowledge to adequately define the relevant process parameters for a given output. For smelting of waste oxides, this requires the quantification of the raw material tonnages, oxygen and nitrogen tonnages, hot metal and slag output, offgas, and dust and sludge generation rates. In addition, the design of the raw material preprocessing equipment, smelting reactor, offgas cooling and cleaning system, and casthouse will have to be specified.

The required hot metal production defines the raw material, oxygen, and nitrogen requirements in addition to the slag, gas, dust, and sludge outputs based on rigorous energy and materials balances. A good understanding of the postcombustion degree, heat losses, dust generation, and recycle, necessary for accurate estimations, has been obtained from the pilot plant work as shown earlier.

The design of the smelting reactor is based on sound principles. The volumes of the required amounts of metal, slag, char, and free space are based on the process fundamentals and are well defined. The dimensions of the vessel (diameter, height, and shape) are based on critical process parameters such as the superficial gas velocity, oxygen distribution ratio, and slag thickness.

The gas handling system is designed to control the offgas temperature such that zinc, lead, alkalis, and halides are not captured in the cyclone and are not deposited in the offgas ducts. The temperature of the gas entering the cyclone will be controlled by using water sprays or oxygen. The cyclone will capture most of the carbon and at least half the iron. The venturi scrubbers will clean the gas such that the solids are completely removed.

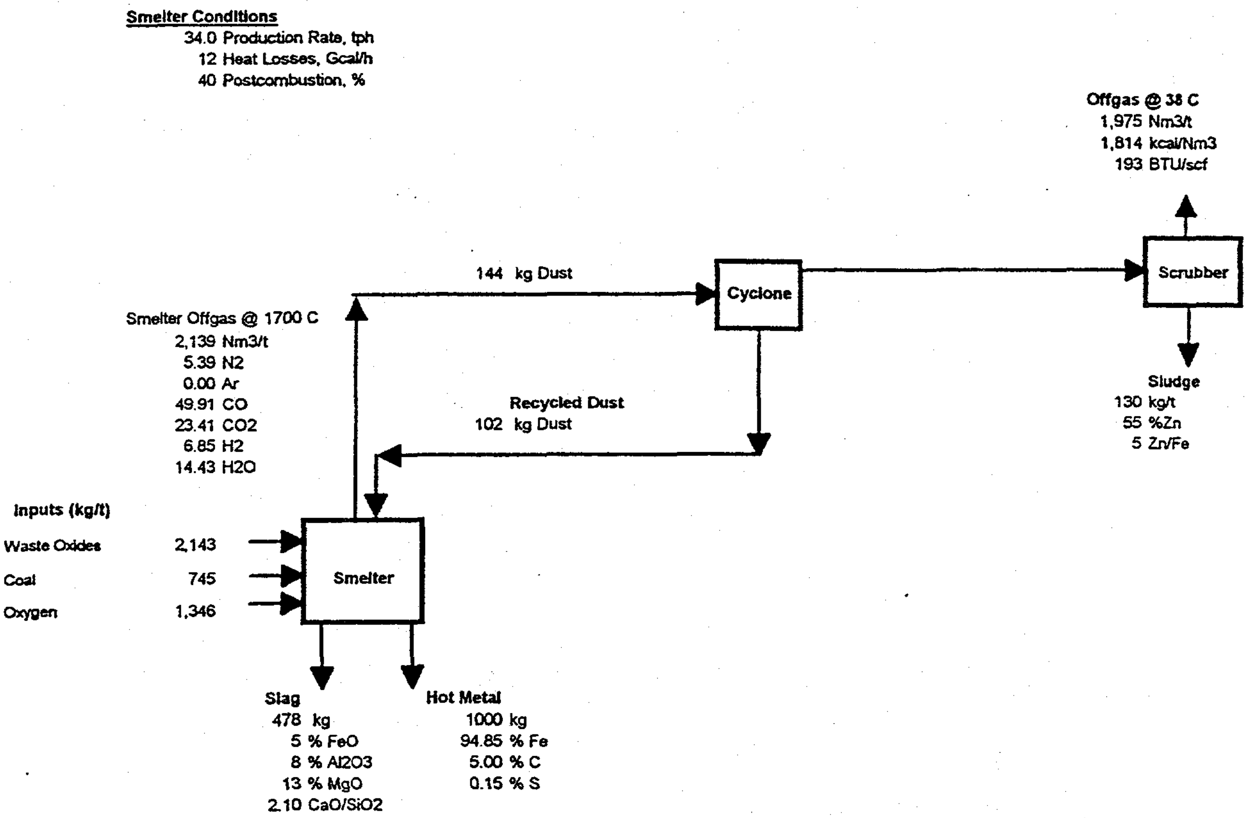
In summary, it can be said that the extensive and comprehensive nature of the investigations conducted at laboratory and pilot scale has resulted in a thorough understanding of the process. The key process phenomena have been studied in detail and are well understood. The scaleup criteria are well defined, and the design of a demonstration plant is based on a solid foundation of fundamental and practical knowledge.

The waste oxide demonstration plant was designed to process about 533,000 tpy of dried waste oxides, which normally contain up to 50% moisture. This will avoid the landfilling of about one million tpy of BF, BOF, and HSM wastes. At the same time, the smelting process will recover about 256,000 tpy of carbon-saturated molten iron. About 122,000 tpy of slag, which can be used in construction applications, will be generated. The thermal value of the cleaned offgas could be used in slab reheating furnaces as a partial replacement for purchased natural gas or used to produce steam. About 33,000 t of zinc-rich sludge will be generated and sold to zinc producers for its recovery.

Energy and Materials Balances

Figure 29 shows the projected flowsheet for the demonstration plant. Energy and materials balance calculations were conducted for an annual hot metal production rate of 250,000 metric tons, such that all products leaving the plant, including the sludge, will be usable. The results of these calculations, important flowsheet considerations, and design of the smelting reactor are discussed.

Figure 29 – Waste Oxide Demonstration Plant Flowsheet



NOTE: Units are per metric ton of HM unless otherwise specified

The raw material composition of the waste oxides to be processed is shown in Table 15. The waste oxides will be preprocessed such that the charge to the smelter is dry micro-agglomerates containing 3% moisture. The base coal used in smelting of the waste oxides was taken to be "run of mine" medium volatile coal containing about 20% volatile matter. The coal charged to the smelter will be thermally dried to 2% moisture. The coal composition is also shown in Table 15.

Table 15 – Raw Material Composition

	Waste Oxides	Mid Vol Coal
SiO2	4.44	1.8
Al2O3	1.23	1.2
CaO	10.47	0.6
MgO	3.02	0.1
FeO	26.69	0
Fe2O3	27.3	1.4
Fe met	7.2	0
C	12.21	85.5
S	0.36	0.8
H		4.3
N		1.3
O		3
ZnO	4.33	
PbO	0.43	
Total Fe	47.07	0.98
Total Gangue	19.16	3.70

The flowsheet is based on producing a sludge with a zinc-to-iron ratio of five. This will require two blends of waste oxides. The base waste oxide blend for the specific location under study does not contain enough zinc to produce a sludge with a zinc-to-iron ratio of five. Therefore, the sludge generated during operation with the base blend will be mixed with the base blend to produce a second mix with a higher zinc content. The second blend will consist of about 6% smelter sludge and 94% of the base waste oxide blend. The operating time will be split almost equally for the two blends. The flowsheet shown in Figure 29 represents an average for operation with the two blends.

Operating Parameters

The values used in the energy and materials balance calculations, for the critical operating parameters, are shown in Table 16. The aim postcombustion for operation with the low volatile coal is 40%. At the pilot plant, stable operation at 38% PC with a medium volatile coal was demonstrated. Based on the pilot plant results, the target of 40% PC for the demonstration plant, operating at higher pressures, should be readily achievable. Further, the results of the Japanese

DIOS Smelting Project at the Keihin pilot plant have confirmed the PC level and the projected fuel rate.[14]

Table 16 – Operating Parameters for Demonstration Plant

1.	Postcombustion (%)	40
2.	Heat Losses (Gcal/h)	12
3.	Offgas Temperature (C)	1700
4.	Metal/Slag Temperature (C)	1525
5.	Carbon in Hot Metal (%)	5
6.	FeO in Slag	5
7.	Smelter Dust (% of dry feed)	5%, (50% C, 45% FeO, 5% Gangue)
8.	Smelter Dust Recycle	95% of Carbon Dust, 50% of Iron Oxide Dust
9.	Iron Oxide Feed	3% Moisture, No Binder
10.	Coal Moisture	2%
11.	Heat of Dissociation of Coal	0
12.	Carbon Loss in Slag	0
13.	Flux Additions	None
14.	Bottom Stirring (Nm^3/h)	2000
15.	Oxygen Purity (%)	95 (Balance Nitrogen)

The heat losses used for the demonstration plant smelting reactor were based on the heat fluxes measured at the pilot plant. The heat losses to the refractories and water-cooled walls of the demonstration plant smelter were calculated to be 12 Gcal/h. In addition, the superheat in the offgas and dust was 6.6 Gcal/h. The total heat generated in the smelter is about 116.7 Gcal/h, and the resultant thermal efficiency is about 84%.

The aim metal and slag temperature during operation is 1525 °C. At the pilot plant trials, the aim operating temperature was 1550 °C. The reason for the higher aim temperature was due to high MgO content of the slags. However, with the improved lining design and extended operation, the MgO levels are expected to be lower. Thus, the lower aim operating temperature is consistent with other technical objectives.

The carbon in the hot metal was taken to be 5% at 1525 °C, and the slag will contain 5% FeO. The projected hot metal sulfur content at tap is 0.15%. This is based on a model developed using pilot plant results and the thermodynamic and kinetic behavior of sulfur in smelting. This model has also been successfully used to predict the sulfur content of the DIOS process.

The smelter dust rate and chemical composition were based on the pilot plant results. The dust generation from the smelter was taken to be 5% of the dry solids input. Carbon in the dust was 9.8% of the fuel input, while iron oxide in the dust was 3% of the waste oxide input. The cyclone efficiency for carbon and iron was taken to be 95% and 50% respectively, which is consistent with pilot plant results.

The purity of oxygen was specified to be 95% with the balance being nitrogen. The operating time for the smelter was taken to be 95% of 330 days. The time for relines and maintenance was taken into account. The estimated operating time annually is 7524 hours.

Fuel and Oxygen Rate

The hot metal production rate from the smelter was based at 34 tph, resulting in an annual production of about 256,000 tons. The coal rate per ton of hot metal produced is estimated to be 745 kg, while the corresponding oxygen rate was calculated to be 1346 kg/t. These values are lower than those demonstrated at the pilot plant when operating with mid vol coal. The lower fuel and oxygen rates are explained by the differences between operation at the pilot plant and that anticipated for the demonstration plant. At the pilot plant, agglomerated waste oxides containing 10% binder were used. The waste oxides for the demonstration plant, which will be micro-agglomerated without a binder, contain less gangue and more carbon and iron. Smelter dust containing a substantial amount of carbon and some iron was not charged back into the smelter during operation with coal. The PC level for the demonstration plant is about 5% higher, and the heat losses per ton of hot metal are substantially lower. With scaleup, the heat loss per ton of hot metal produced is lowered.

The estimated fuel rate and oxygen rate for a hot metal production rate of 35 tph based on AISI pilot plant results are consistent with published data on DIOS. In addition, it must be remembered that the current estimates are based on experiences at the pilot scale, with the Keihin pilot plant being the largest at a hot metal production rate of 22 tph. It is envisioned that, in a continuously operating commercial facility, improvements will be made over time such that the process performance is enhanced. Some of these improvements will undoubtedly come from improved raw material preprocessing and distribution, better refractory maintenance practices, improved blowing practices and other operating practices, and the development of superior process sensors and control systems.

Hot Metal Quality

One of the main advantages of the postcombustion smelting technology for waste oxide recycling is that the iron units are recovered as hot metal. The metal produced is carbon-saturated with low levels of Si, Al, Mn, and phosphorus. The aluminum and silicon contents in hot metal produced in the smelter are minimal, and the manganese content is much lower than that produced in the blast furnace.

The sulfur content of the hot metal, at tap, is expected to be about 0.15%. Postsmelting desulfurization experiments conducted at the pilot plant have shown that the hot metal sulfur was reduced to a fifth of the cast hot metal sulfur. This was because the smelter slag was far from saturated in sulfur. This approach will be used at the demonstration plant to lower the sulfur in the hot metal leaving the plant such that it can be blended with blast furnace hot metal and charged to the BOF. In the event that slag-metal stirring does not reduce the sulfur content to that required, injection of lime, which is a proven technology, will be used.

Thus, the hot metal leaving the waste oxide recycling demonstration plant will be carbon-saturated, molten, and low in sulfur, making it a much better feed material to the BOF as compared to scrap or granulated/pigged iron.

Smelter Slag

About 478 kg of slag will be produced per ton of hot metal. Annually, this will amount to 122,000 t. The slag cast from the smelter will have a lime-to-silica ratio of about 1.8. The MgO content is expected to be about 13%, while the estimated alumina content is 8%. The sulfur content of the slag after desulfurization is projected to be 0.8%. Based on the tests conducted on the slag from a desulfurization experiment, it can be concluded that this slag will be suitable for use in road construction applications, provided the refractory lining performs as expected. In addition, the leaching of sulfur under extended exposure to water, a phenomenon associated with blast furnace slag, did not occur with smelter slag used in a hot metal desulfurization test.

Smelter Offgas

The gas exiting the smelter is dust-laden and is cleaned in two stages. In the first stage, a hot cyclone is used where most of the carbon and half the iron and gangue are removed. The relatively cleaner gas that exits the cyclone is then passed through venturi scrubbers where the final cleaning takes place. The solids are removed as sludge, while the cooled and cleaned offgas can be used as fuel.

The fuel value in the cleaned gas is estimated to be 1814 kcal/Nm^3 (193 BTU/scf). This gas contains less than 50 ppm, sulfur (equivalent H_2S), which is about twenty times less than that in desulfurized coke oven gas. Further, it contains very low amounts of hydrocarbons and nitrogen oxides. The volume of the gas exiting the scrubber is estimated to be 1975 Nm^3/t or 67249 Nm^3/h. The offgas could be used in slab reheating furnaces at the host site to partly replace purchased natural gas and desulfurized coke oven gas or for steam generation.

Smelter Sludge

A critical advantage of the application of postcombustion smelting technology to waste oxides containing zinc, lead, alkalis, and halides is the ability to process them in the manner desired. To make the sludge suitable for zinc recovery, it should have a zinc-to-iron ratio in excess of five and must be low in alkalis and halides. The pilot plant results have clearly demonstrated that zinc reports to the scrubber sludge and that zinc-to-iron ratios in excess of five were achieved. In addition, the alkalis and halides reported to the contact water rather than the sludge. At the demonstration plant, about 33,000 t of sludge with a zinc-to-iron ratio of five will be generated. This sludge will be suitable for zinc recovery, and a letter to that effect has been received from Canadian Electrolytic Zinc, Ltd., based on the work of their Noranda Technology Center.

ECONOMIC ANALYSIS

The pilot plant trials showed that a variety of steel plant waste oxides can be successfully smelted to produce liquid hot metal similar to that from the blast furnace that can be converted to steel in a conventional basic oxygen furnace (BOF). In addition, the smelter produces a valuable gas that can be exported and used as a replacement for coal, natural gas, and oil in other energy-consuming processes. Slag from the smelter can be used for road aggregate, and the sludge from the smelter's gas cleaning system will be high enough in zinc to be sold to a primary zinc producer. Therefore, the smelting process converts steel plant wastes that must normally be disposed of with a cost and with some penalty to the environment into products that have value.

Although the preparation of the waste oxides will vary somewhat depending upon their source, it will generally consist of the drying of high-moisture-content sludges and the blending and agglomerating of several materials to produce a smelter feed that is reasonably uniform in composition and can be handled in the stock bins and the feed system. The capital and operating costs of the preparation system are included in the economics discussed below.

The economics presented herein are for a smelting plant sized to produce 250,000 metric tons of hot metal per year. The types of sludges and dusts that are available to be smelted are for a generic steel plant. The waste oxide blend composition is similar to that suggested to be available for commercial operation, except that the zinc concentration was altered to reflect a higher zinc load available from a producer who recycles a considerable amount of galvanized scrap.

The operating costs, credits, and cost avoidances are all expressed per metric ton of hot metal. The process elements such as coal rate and costs are shown in Table 17. The unit costs are representative of those that might be obtained in several geographic locations. Costs and/or usage rates such as electrical power are based on the Mannesmann Demag report on the AISI ironmaking process. Other usage rates are based on pilot plant experience with appropriate scaleup factors and on estimates made by experts in specific fields, such as material preparation and refractories.

The total operating cost, as shown in Table 17, is about $140 per metric ton of hot metal ($/t). The total operating cost is offset by a number of credits as also shown in Table 17. These include a credit of about $30/t for export gas at $2.50 per million (MM) Btu. Fuel for drying the oxides and coal has been deducted.

Credit of $72/t of hot metal is shown for avoiding the cost of landfilling the waste oxides. This derives from a $30 per metric ton cost avoidance for landfilling the waste oxides accepted by steel companies in several geographic locations and expected to escalate at a rate of 10 percent per year.

Credit of $56/t is shown for the sale of sludge. The waste oxide feed is assumed to be sufficiently high in zinc to produce a sludge with a zinc-to-iron ratio greater than five. The zinc-to-iron ratio and other qualities and specifications necessary to make the sludge a salable product have been approved by Canadian Electrolytic Zinc, Ltd., a major zinc producer, at a price of $425/ton of contained zinc.

The net operating profit from the smelter operation is projected to be $158/thm. This derives from the $140/t operating cost offset by the credits for gas, landfill avoidance, and sludge sale. The total profit for the plant is about $39.6 million per year that would provide a rate of return of about 34% on the estimated $75 million plant cost.

Table 17 - Steel Plant Waste Oxide Smelting Plant
Hot Metal Costs - Commercial Operation

Production Rate, tph	33.2
, tpy	250,000
Operating Rate, %	85.9
Waste Material Processed, tpy (dry)	509,750
, Investment, MM$	75
,$/Athm	300
,$/At Waste Oxide	147

	$/Unit	Units/thm	$/thm
Raw Materials			
Misc. Waste Oxides (dry), t	0.00	2.039	0.00
Coal @ 5% H_2O, t	60.43	0.849	51.33
Oxygen, t	31.30	1.402	43.88
Total Material Cost			95.22
Electric Power, Kwh	0.05	30	1.50
Refractories, thm	3.78	1	3.78
Cast House & Ladle Refractories, thm	1.25	1	1.25
Nitrogen, t	9.06	0.263	2.38
Air, M^3	0.005	8.8	0.04
Cooling Water, y	355,000	1	1.42
Operations & Casting Labor, y (18 People)	1,120,636		4.48
Material Preparation Labor, y (17 People)	1,056,523		4.23
Maintenance Labor, y (12 People)	744,307		2.98
R & M Materials @ 2% of Investment			6.00
Spares @ 2 % of Investment			6.00
Sublance Tips & Maintenance, thm	4.96	1	4.96
Desulfurization			
Hot Metal - Ferro Silicon Added, kg	0.66	3	1.98
Slag Removal - Pit to Pit, t	2.13	0.349	0.74
Slag Disposal Cost, t	1.42	0.349	0.50
Plant Operating Expense, y	532,500		2.13
Total Operating Cost			139.59
Credits			
Offgas Credit, MMBtu (100% Utilized)	2.50	11.84	29.61
Landfill Credit, t (@ 15% H_2O)	30.00	2.399	71.96
Sludge Sale, t	267.00	0.211	56.34
Total Credits			157.91
Operating Profit with Hot Metal @ $140/t*			158.32
Total Operating Profit, $MM/y			39.58

BASIS & NOTES:

1. Hot metal desulfurized to 0.04% with smelter slag.
2. Offgas recovery @ 90 %. Excludes fuel for coal (7 to 2%) and oxide drying (15 to 3 %) @ 4 MMBtu/t H_2O.
3. Smelter dust rate @ 6% of material feed.

The economics show that the smelting of steel plant waste oxides can be a profitable venture. The profits will vary somewhat, depending upon geographic conditions and on the type of steel plant waste oxides being smelted. However, following completion of this demonstration program and verification that the process meets the design criteria, it appears clear that a return on investment (ROI) of 35 - 40% would be obtained for a similar plant. The Technical Advisory Committee for the Waste Oxide Recycling Program has identified six to eight locations in the United States where such plants could be built economically in the future.

ENERGY ANALYSIS

The smelting of steel plant waste oxides can result in considerable energy saving compared with the conventional coke oven/blast furnace method for producing hot metal. The net life-cycle energy required to produce a metric ton of hot metal in the blast furnace including the coking operation is about 22 MMBtu per metric ton (MMBtu/t) as shown in Table 18. This can vary from about 20 to 24 MMBtu/t, depending upon the age and condition of the facilities and the operating practice employed. The energy consumption includes that for mining and transportation of coal and ore and for the production of iron ore pellets.

The energy for the smelting of waste oxides for the case presented in the economics section of this report is also shown in Table 18. The energy required to produce the oxygen is included. Energy credits are taken for the export gas produced by the smelter and for the carbon contained in the waste oxide smelter feed. The latter recognizes that the carbon in the oxides offsets the carbon requirements from coal that would otherwise be required. For this case, the energy required is 16.97 MMBtu/t for a saving of about 23 percent, or about 4.98 MMBtu/t. This is a significant energy saving over that required to produce hot metal in the conventional manner. (No energy credit has been taken for avoiding the energy for shipping waste to landfills nor penalty for shipping off-site wastes to the recycling plant.)

About three million metric tons of steel plant waste oxides are disposed of each year. If all this material could be smelted to produce about 1.5 million metric tons of hot metal, displacing blast furnace hot metal, the energy saving would be about 7.5 trillion (0.008 quad) Btu per year.

Table 18 – Energy Requirements for Producing Hot Metal

		CO/BF		Steel Plant Waste Oxide Smelting	
	MMBtu/Unit	Units/thm	MMBtu/thm	Units/thm	MMBtu/thm
Coal, t	31.26	0.70	21.76	0.807	25.23
Waste Oxides, t	3.47			1.899	6.58
Oxide Pellets, t	2.89	1.48	4.29		
Gravel and Limestone, t	0.29	0.25	0.07		
Electricity, Kwh	0.0095	45	0.43	30	0.29
Oxygen, t	2.93			1.127	3.30
Credit for Export Gas, MMBtu	1.00	-4.60	-4.60	11.84	-11.84
Total			**21.95**		**23.55**
Credit for Carbon in Waste Oxide, MMBtu/thm					-6.58
Net Energy Consumed, MMBtu/thm					16.97
Energy Saving, MMBtu/thm					4.98
,%					23

NOTE: Steel plant waste oxide energy content includes carbon.

ENVIRONMENT, SAFETY, AND HEALTH ISSUES

An Environmental Impact Assessment for the proposed demonstration plant to smelt steel plant waste oxides to produce usable products of hot metal, slag, and fuel has been prepared.

The report reviews the potential environmental effects of the proposed plant on air, surface water, groundwater, and soils. A comparison of Canadian and U. S. regulations has been conducted. The plant would be designed to meet the most stringent of the two, to be able to prove compliance in either country. In addition, an evaluation of impacts on the natural surroundings and local populace is also included. The major areas of concern and the conclusions reached are as follows:

Potential Impact on Air Quality by the Addition of a New Source

Gases. Stack sampling tests at the pilot plant showed that the major pollutant would be sulfur dioxide that would be formed when smelter offgas is burned at the flare stack or at other consuming locations such as reheat furnaces. The small amount of hydrocarbons present in the gas will be destroyed during combustion. The sulfur dioxide content of the gas is estimated at 40 ppm_V after combustion. The effect of this discharge to the atmosphere was evaluated using mathematical models approved by regulatory authorities. It was found that the impact of sulfur dioxide is within the applicable standards for the host site.

Particulates. Particulates in the smelter offgas will be limited to 0.01 grams per normal cubic meter by proper design of wet scrubbers. Similarly, particulate discharges from conveyor transfer points and the casthouse will be controlled using appropriately-sized suction fans and hoods connected to a baghouse. As above, modeling of these discharges indicates that the impact of particulates is within the acceptable standards for the host site.

Overall air emissions are significantly less, per ton of hot metal, for the waste oxide smelter than for a typical coke oven/blast furnace facility, as shown in Table 19.

Table 19 – Air Emissions (Kg/tHM)

Process	Coke Oven/Blast Furnace	AISI Waste Oxide Smelting
Particulates	0.15	0.13
NO_x	0.69	0.02
SO_2	2.5	0.16

Potential Impact on Surface Water Quality via Noncontact and Contact Water

Noncontact Water. Noncontact water will be used to cool the oxygen lance and other cooling members. The existing system consists of appropriate cooling towers, pumps, and hot and cold wells.

Contact Water. Water will be used in scrubbers to remove particulates and to condense volatile metals such as zinc. The sludge collected from the scrubbers will be sold to a primary zinc producer. Sodium, potassium, chloride, and fluoride contained in the smelter feed will report to the contact water. A separate water treatment system will be installed to control the buildup of these compounds to prevent scaling and corrosion. Blowdown from this plant will be treated in either the host company's existing terminal treatment plant or a new treatment plant and should have no appreciable impact on the receiving water bodies.

Potential Impact to Human Health

Adequate air emission controls will be installed to insure that the air quality will meet local air quality limits. Similarly, blowdown water will be treated in the existing terminal treatment system to comply with effluent standards. Furthermore, the plant will be designed to conform with worker health and safety regulations regarding fugitive dusts and other worker activities, including the handling of hot metal.

During the demonstration operation, comprehensive tests will be conducted to completely characterize the environmental impacts of the smelting plant. If violations of existing regulations are observed, the plant will be modified as appropriate to insure compliance with environmental regulations.

COMPETITIVE TECHNOLOGY

This section is authored by P. J. Koros.

Technologies currently in use or at advanced stages of development for processing of materials that until now have been considered steel plant waste oxides, i.e., fine particulate dusts and sludges captured in baghouses, precipitators, scrubbers, and filters, can be classified into two broad categories:

Internal Reuse, that is, charge part of blast furnace, BOF, ladle metallurgy, and rolling mill iron-rich oxide wastes back into one of the iron and steelmaking process steps. As discussed below, this approach generally leads to only partial, limited recovery of iron and carbon units and to waste of the valuable zinc also present at increasingly high concentrations. Energy and reductant are generally provided by the steelmaking process at a penalty in productive capability for BOF operations with limited hot metal supply.

Dedicated Processes for reduction and separation of the metallic components of the iron-rich dusts and sludges. Usable forms of iron, zinc, and the process slag are produced. In the AISI smelter case, the process gases have intrinsic energy value. These technologies rely mostly on carbon forms for energy and reduction. Although significant effort has been expended to implement plasmas and a commercial venture has recently been announced, plasma systems have seen limited technical and economic success due to costs and problems in gas collection and, until now, have been used only for dusts collected from EAF and AOD units producing stainless steels.

The current state of development and, to the extent practicable, the economics of these processes are reviewed below. Specific process economics depend on local conditions, such as landfill costs and the hot metal/scrap cost balance for each plant. It is concluded that:

- Allowing for costs for briquetting, production penalties, loss of zinc and iron units, and the continued need for landfilling, the internal reuse approach can be considered only as a costly, limited solution to the basic problem.

- Currently there are only two processes, other than the AISI smelting technology, with potential for consumption of the oxides generated at integrated plants: ROMELT and INMETCO. ROMELT has a major deficiency in energy use and discharge (and scaleup is difficult to quantify), while INMETCO has yet to be operated as a total process with zinc-bearing dusts/sludges. As far as can be forecast at this time, total technology favors the AISI process.

Internal Reuse

This approach for reduction of landfill volume and for recovery of some iron units has seen many forms throughout the years: agglomeration with binders and by cold bonding, followed by return to one of the iron and steelmaking process steps. Current North American examples include the programs at Stelco-Hilton and Lake Erie Works,[15] at Inland Steel,[16] at USS-Mon Valley Works, and at Great Lakes Steel.[17] In Europe, Voest-Alpine[18] and Klöckner[19] are the examples. Nonetheless, there are technical, operational, environmental, and economic limitations (penalties) to this approach.

Blast Furnace. Cold bonded pellets made of blast furnace dust, even at their highest strength, are suitable only for limited use (5 - 7% of burden) in blast furnaces, due to loss in bed permeability and, thus, iron production. Stelco[15] and USS-Gary have experience with this approach. Use in cupolas has been proposed as part of the PelleTec Process, but the only use has been with low zinc materials in a small (5t/hr) cupola in India.

- Zinc-bearing steelmaking dusts can be charged only into the steelmaking units due to deleterious effects of zinc in blast furnaces.

BOF. The endothermic reduction of the oxides causes an increase in hot metal consumption and, thus, loss of production in hot-metal-short BOF shops. One permutation to this is the possibility to agglomerate only the carbon-bearing blast furnace oxides, and assuming that carbon in the blast furnace oxides behaves like carbon from hot metal, there would be a reduced penalty in hot metal use for the reduction process, Table 20.

Table 20 – Effects of Waste Oxides in BOF Charges

BASIS: 10% BINDER (PORTLAND CEMENT)

	Oxides			Blow Time	Scrap	Fluxes	Hot Metal
Case	% Fe	%C	t/t Steel	Change -Minutes	t/t Steel	t/t Steel	t/t Steel
Base					0.306	0.046	0.837
BOF Dusts	57.2	0.35	0.028	-0.70	0.241	0.048	0.886
BF Dusts							
HSM Sludges	36	26	0.028	+2.3	0.298	0.050	0.836

Environment. Environmental limitations of these approaches are serious as, even if the hot metal ratio loss in the BOF can be tolerated, enrichment in zinc of the waste gas/oxide system would become intolerable and blowdown to landfill would become necessary. Thus, total recycle/recovery of all Fe and Zn units is not possible; Stelco's model[15] indicates 60% is the maximum reuse rate for BOF sludges to avoid unlimited buildup of zinc in the sludge. The buildup in lead that accompanies the rise in zinc content can turn the catch hazardous for lead as determined by the EPA leachable lead test (TCLP). Similarly, if the approach is to briquette/charge to the BOF only the BF-generated (low zinc) oxides, then BOF oxides remain waste products, that is, go to landfill. In some BOF shops, the use of agglomerated oxides has led to slopping,[17] another source of environmental problems. The elegant approaches reported by Voest-Alpine,[18] and by Klöckner[19] for a KMS installation, lead to a different outcome: converter dusts are separated by size with the fine fraction, either hot briquetted for recharge[18] or used by bottom injection[19] into the KMS vessels. The recirculating zinc load is allowed to build up[18] until 25% Zn is reached, at which level a blowdown to a Waelz kiln operation is made; thus, the Fe and Zn units are recovered but at the penalty of a 3:1 loss in scrap melting. However, experience (LTV Steel) shows that conventional BOF shop environmental systems, precipitator or scrubber, have difficulty in coping with zinc levels above 7 - 11%, so the Voest-Alpine approach may have other aspects to address to make it practical.

Economics. The major economic penalties from return of waste units to the iron and steelmaking process come from (a) the cost for agglomeration ($35 to $50/NT of waste oxides) and (b) the increased use of hot metal in the BOF process for hot-metal-limited shops. Benefits accrue from a reduction in landfilling costs and, in shops with excess hot metal, the replacement of expensive No. 1 scrap grades by hot metal.

Dedicated Processes

The two hot metal processes, besides AISI smelting, that have met the test of at least partial pilot plant operation are INMETCO[20, 21] and ROMELT.[22] Although there are substantial differences among the three, there are common features: capability to consume all steel plant waste oxides and to produce separate, usable forms of iron (liquid hot metal), zinc (oxides), and slags. Thus, these meet the requirement of providing for substantial, near total, elimination of the need for landfilling, although the energy efficiency and composition and value of tail gases differ greatly.

Other processes have been proposed, and even tested, for utilization of waste oxides. Two of these have seen limited use (Sumitomo[23] and Thyssen-Lurgi[24]), and a third (Russian) process has seen pilot tests. All these have a major disadvantage in that their iron-bearing products are oxides suitable only for feed to sinter plants, which are generally used in Japan and Europe but of limited interest in North America.

Process overviews and economics are discussed below. Table 21 provides a basis for comparisons.

Table 21 – Comparison of Waste Oxide Processes

	Feed			Products			Reductants		Tail Gas
	BF	BOF	HSM	HM	SLAG	Zn*	Type	Rate t/t HM	Energy Value
AISI	X	X	X	X	X	M	Coal (MV)/Coke Breeze BF dust Carbon	0.7	15 MM Btu/NT
ROMELT	X	X	X	X	X	L	Coal (HV)	1.5	U/K
INMETCO	X	X	X	X	X	H	B.F. Carbon a/o Coke Breeze; 500 Kwh/t HM	Nil to 0.3 t/t	Nil

*Zinc value indication - based on Zn/Fe ratio in catch.

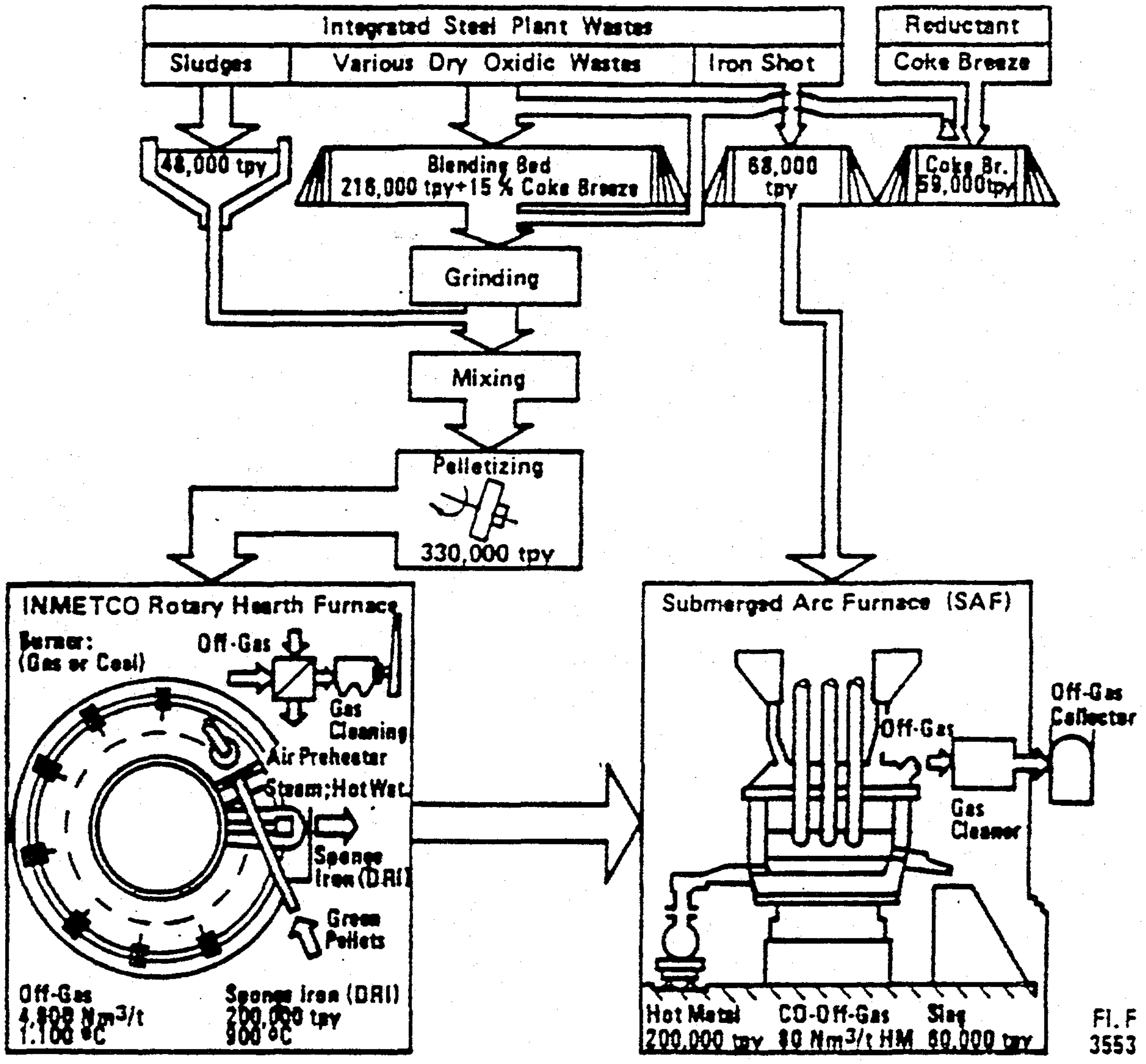
INMETCO. This process, initially developed by International Nickel, is in commercial use at the Ellwood City, PA, plant for treatment of EAF (stainless) and AOD baghouse dusts and for grinder swarf. Mannesmann Demag has analyzed several scenarios by which INMETCO process plants could be installed to serve BF-BOF-CC-HSM complexes. The process steps have been simulated individually, but a whole plant has not been operated with oxides from an integrated plant.

The process flowsheet is shown in Figure 30. Oxides from the plant and coke breeze would be dried, blended, and formed into green balls with sufficient strength to be rolled onto a rotary hearth furnace. The furnace could be fired with natural gas, coke oven gas, or oil. Carbon in the blast furnace dusts and makeup coke would reduce the iron oxides by 85 - 95%. Zinc and lead (and alkali) are reduced and leave via the gas phase where they are reoxidized to be drawn off into a baghouse with the furnace waste gases. The partially reduced and strengthened balls are discharged from the hearth and moved into a submerged arc smelting electric furnace. The SAF discharges hot metal and a slag usable like BF slag. The dust catch from the smelting furnace is returned to the front of the process; this promotes recovery of the iron units and results in a very high zinc-to-iron ratio in the catch from the rotary hearth furnace (high value for zinc sale).

Environmentally, this process is expected to produce/recover all the iron (as hot metal) and the zinc and oxidized lead units as oxides, captured dry with the alkalis and halides or as sludge without the alkalis and halides. The slag from the electric smelter is to be usable as road aggregate. The process gases, from the rotary hearth furnace and the smelter, are expected to be low in SO_2 in cases when the blast furnace dusts/sludges provide all the reductant to the process.

Energy consumption for a typical steel plant waste feed is reported as about 500 Kwh/tHM for the smelter. Coke breeze consumption is dependent on the carbon input from the blast furnace products. Range is from nil to 350 kg/tHM.

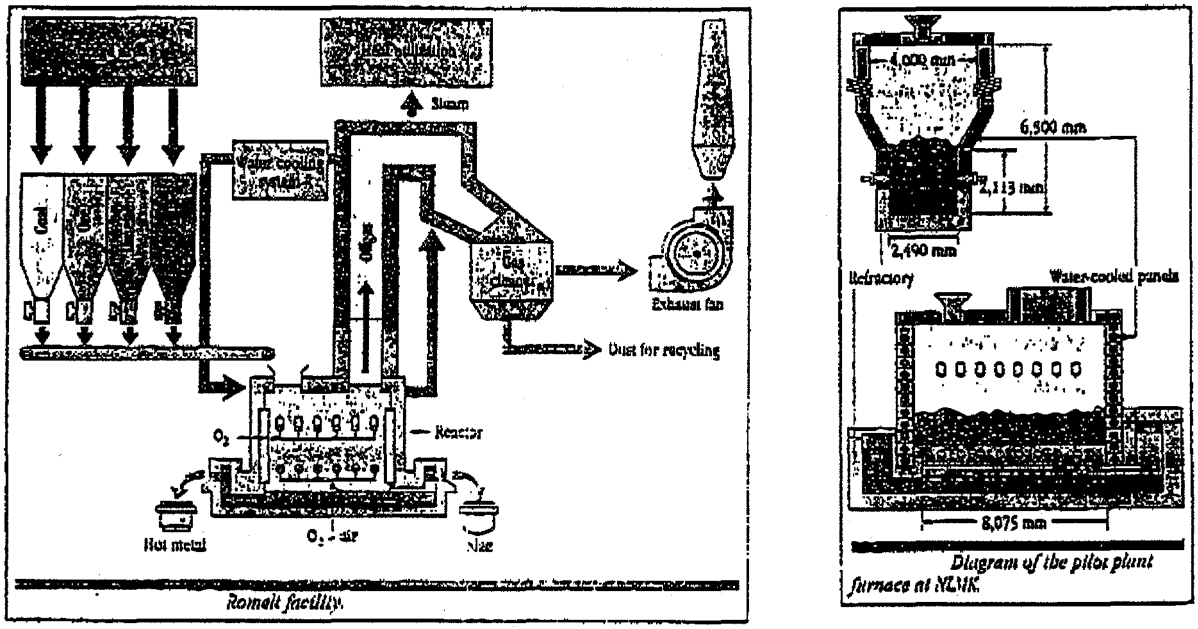
Figure 30 – INMETCO Process Schematic



ROMELT. Initially developed for smelting of copper and nickel sulfide ores (then known as the Vanyukov Process), in the early 1980s the Moscow Institute of Steel and Alloys (MISA) adapted the process concept to smelting of iron ores. A pilot facility was built (1985) at the No. 2 BOF shop of the Novolipetsk Steel Plant. In the 34 operating trials to date, various iron sources have been smelted/melted, culminating with the AISI-DOE-sponsored tests in 1994. By 1992, MISA personnel realized that the only application for the process would be in waste oxide processing, and several runs have been conducted in this mode.

Smelting reactions occur in a horizontal, rectangular vessel, using a violently-stirred slag as the reaction medium. Furnace pressure is slightly below atmospheric. The process flowsheet is illustrated in Figure 31. Coal (the source of the carbon reductant) and all other feed materials are introduced by gravity through a funnel. Slag agitation is obtained by introduction of oxygen-enriched air through tuyeres blowing into the slag with partial postcombustion of the CO and H_2 generated in the slag by oxygen blown through an upper row of tuyeres and by air drawn in due to the negative pressure. Contrary to the use of foaming slags for heat recovery, such as for the AISI and the DIOS processes, in the ROMELT furnace the slag is similar to that in blast furnaces (low FeO, slightly acid, glassy appearance), and heat transfer to the slag is by way of heat absorption by the large surface area of the slag droplets thrown into the free space. With HV coal, the postcombustion level attained in the gases leaving the furnace outlet is of the order of 45 - 50%, but at the slag interface, postcombustion is near 30%. The energy generated in going from 30% to 45 - 50% is used mostly to heat the gases and the water-cooled jacket and is not of value for smelting. At the pilot plant and in the process diagram presented recently, the offgases are fully combusted in the offtake, and the energy leaves the process as saturated steam. The simple materials feeding system, for the 10 - 12% moisture charge, leads to a 3% solids loss via bypass to the waste gas system.

Figure 31 – ROMELT Process Schematic.
Waste gas desulfurization is not shown.



Romelt facility.

Diagram of the pilot plant furnace at NLMK.

The use of high temperature energy in the furnace for drying the charge could be diminished by predrying before feeding through the funnel. The outcome of such a change is difficult to predict because the production rates during the trials witnessed by the AISI team were relatively low; thus, the gas velocities also were low, and chemical analyses of the dust catch are not yet available. In any case, as for the AISI smelter, the switch to HV coal led to a visible change in the color of the dust catch, which indicates a similarity in process behavior; thus, feeding of dry HV coals can be expected to lead to a marked increase in carbon losses. Behavior, i.e., short circuit vs. retention of dry, fine steelmaking dusts when fed by way of the funnel, cannot be predicted.

Products from the process are carbon-saturated, low-silicon hot metal, almost completely free of process slag, low FeO 0.9 VR slag, and sludge and dust captured from the waste gas system. Zn and Pb are present as oxides, but as the process lacks a means to return the Fe-bearing fines (short-circuited and generated) to the smelter, the Zn/Fe ratio in the sludge is low and would be considered low quality for North American zinc plants.

Sulfur level in the hot metal is similar to that obtained in blast furnaces, 0.030/0.07 S. However, because the process gases are fully oxidized, the benefits of zinc gas desulfurization are not available, and the full capital and operating costs for SO_2 removal would be required.

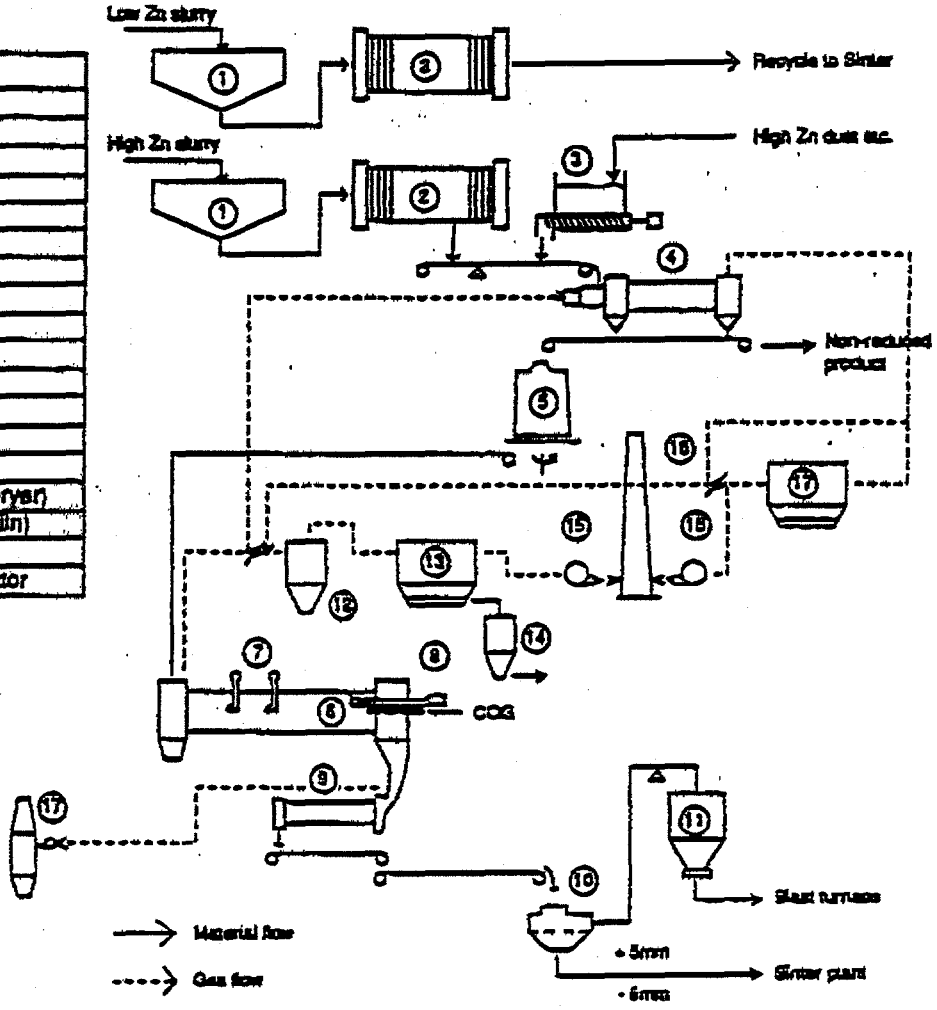
Coal requirements for an operating unit are difficult to project because the whole issue of scaleup effects (what limits production?) is still subject to debate.

Processes Suitable for Sinter Plant Feed

Sumitomo.[23] In use at the Kashima Works, the process is based on a rotary kiln fed with all waste oxides and using coal fines as the reductant, Figure 32. The products are iron oxide (60% -5 mm), which is used as sinter plant feed, with the zinc and alkali units (oxidized) captured in a baghouse and sent to the zinc industry. Kiln slag and the coarse fraction of the iron oxide production is sent to a blast furnace.

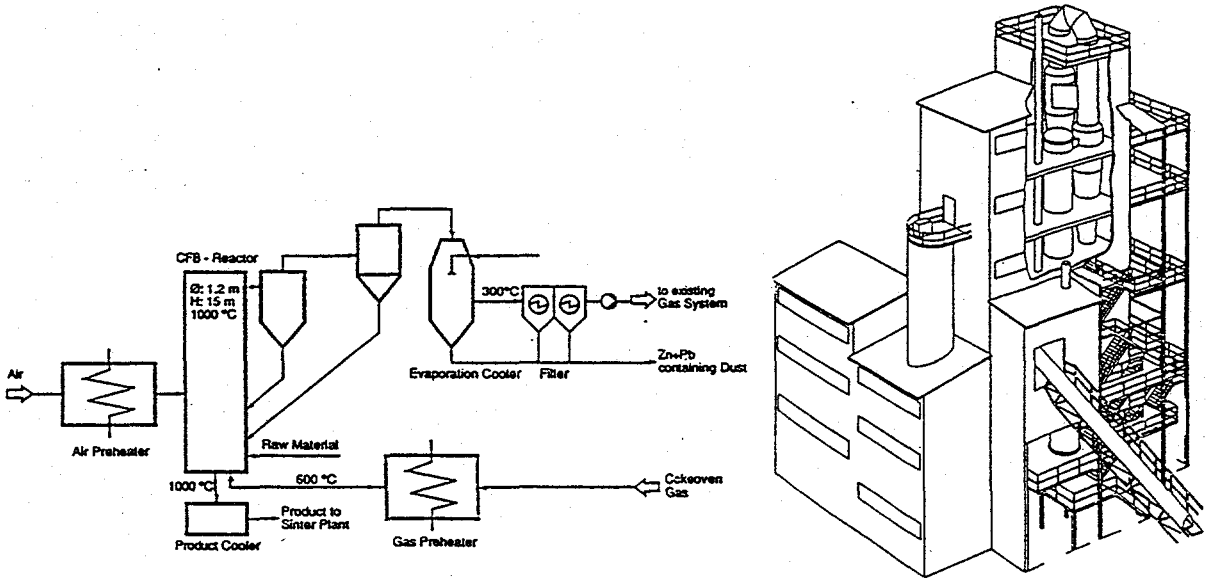
Figure 32 – Sumitomo Dust Treatment Process

No.	Description
1	Thickener
2	Press filter
3	Dust bin
4	Rotary dryer
5	Material bin
6	Rotary kiln
7	Shell fan
8	Boring bar
9	Rotary cooler
10	Vibrating screen
11	Product hopper
12	Cyclone
13	Bag filter
14	Kiln dust hopper
15	Main exhaust fan (Dryer) Main exhaust fan (Kiln)
16	Stack
17	Wet type dust collector



Thyssen-Lurgi.[24] This process, Figure 33, consists of a circulating fluidized bed fed by dried, oil-free steel plant oxides and fine coal. Iron units are removed as FeO for use in sintering, and the Zn, Pb, Na, K, and halides form a complex oxide suitable for processing with a Waelz kiln. A major problem developed in the pilot plant (4t/day) when the hot, gaseous halides attacked the whole unit; after a major, costly rebuild using stainless steel for construction, the pilot plant operated successfully. The actual 20 t/hr plant proposed for approval has not yet been built.

Figure 33 – Thyssen-Lurgi Pilot Plant for Treatment of Steel Plant Oxides (Ref. 24)

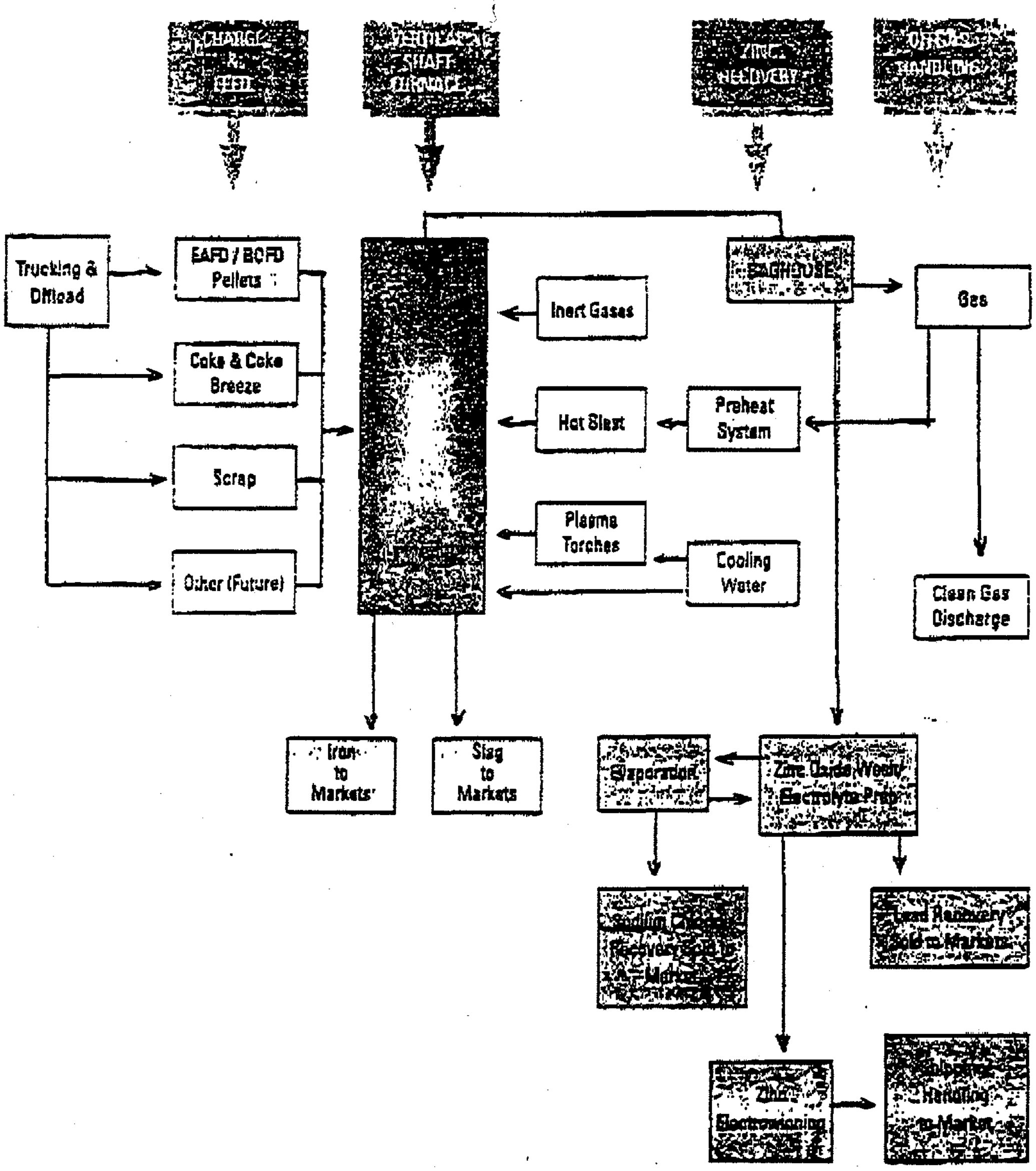


<u>Another Russian process</u>, developed by the Bardin Institute for treatment of zinc-bearing sludges and dusts, consists of heating batches of a mixture of these with coke breeze in a furnace held in a low-grade vacuum. Zinc and lead are reduced and vaporized for collection as oxides (with halides and alkali). The iron-bearing product is considered suitable mostly for sinter feed or for charging into small blast furnaces. However, the indication is that vaporization removes only about 85% of the zinc, so that further use of the iron product may be subject to restrictions. (In a typical sinter plant, vaporization loss of zinc is about 14%.) There is no information on the quality of the zinc catch, that is, on whether it would need prerefining to fit into the North American zinc industry.

Plasma-based Technologies

Plasma-based processes, such as SKF's Plasmadust and Tetronics, have been relegated to treatment of EAF and AOD baghouse dusts because energy costs and difficulties in collection of usable metallic zinc in splash condensers have made these economically attractive only in special circumstances. For SKF, this is for valuable elements like Cr, Ni, and Mo. In the mid 80s, Westinghouse, with EPRI and AISI support, conducted an unsuccessful test of the use of their plasma cupola to smelt oil-laden mill scale. Recently,[25] announcements have been received of a commercial venture (Philip Environmental, Hamilton) for construction of a plasma cupola (Figure 34) for smelting agglomerated (pelletized) EAF and BOF dusts (80,000 t/yr target, capital cost about $435/a.t. of EAF baghouse dust) with recovery of the zinc as oxides in a baghouse. The technical and economic viability of this effort is yet to be demonstrated in view of earlier problems in prevention of iron oxide carry over from cupolas and the claim of new proprietary methodology to convert low Zn/Fe ratio oxides into salable zinc.

Figure 34 – Proposed Flowsheet for Philip Environmental ZPP Process (Ref. 25)



COMMERCIALIZATION

The goals of commercializing the steel plant waste oxide recycling technology and, subsequently, the direct ironmaking technology are paramount. All aspects of any Demonstration Plant Program will be planned and executed to enhance widespread deployment of these energy-efficient technologies on a commercial basis at the earliest possible date.

A wholly-owned subsidiary of AISI, Steel Technology Corporation, pursuant to an agreement with DOE, will facilitate this commercialization. It is clearly understood by AISI that DOE has a strong interest in the early implementation of the results of the demonstration, through commercialization.

Advance planning for commercialization will include publicity activities to condition the potential market for this technology. It also includes identification and protection of intellectual property rights, creation of an organization to carry out commercialization, and linkage with companies that own ancillary technologies, so that these technologies can be offered as part of a total package by the Steel Technology Corporation.

Four drivers favor rapid implementation:

- The rising cost of landfill disposal for waste oxides.
- Existence of large, potentially valuable stocks of previously generated waste oxides.
- Coke shortages that will eventually limit the blast furnace production.
- Increasing demand for virgin iron units.

Waste Oxide Recycling. Currently, more than three million metric tons (on a dry basis) of steel plant waste oxides are generated annually from blast furnaces, basic oxygen furnaces, electric arc furnaces, and rolling mills that could be recycled. Additionally, large amounts of waste oxides have been stockpiled at steel plants, awaiting an economic recovery process. For example, after the demonstration phase has been completed and a proposed plant is operating on a commercial basis, it can smelt waste oxides stockpiled in lagoons and landfills and from current production.

In addition, another three million metric tons of waste oxides are currently recycled through blast furnaces and basic oxygen furnaces after processing through sinter plants, rotary kilns, or other means of agglomeration. As the alternative means for processing waste oxides are retired or displaced, these oxides will become candidates for the AISI lower cost smelting process.

It is believed that this AISI/DOE smelting technology will become the dominant recovery process over the next ten years. Capital cost for a plant to process about 500,000 metric tons of waste oxides will be about $75 million. Depending on local landfill cost avoidances, such a plant could offer profit potentials of up to $30 million or $40 million per year.

The first few plants will likely be similar in size and capacity to the proposed demonstration plant. With continuing success, a few large regional plants processing as much as a million metric tons of waste oxides are likely to be built. Opt-in participants of the current feasibility study have indicated several locations where such plants could be built, including Cleveland, Chicago, Birmingham, Pittsburgh, and Detroit, among others. Thus, within about ten years, five plants processing about 1,000,000 metric tons each are visualized for North America.

World steel production is about 800 million metric tons per year, with the United States steel industry accounting for about 12%. The generation and stockpiles of waste oxides from world steel production are expected to be similar to that in the United States. Thus, an eightfold increase in waste oxide recycling plants might be expected. Clearly, the worldwide market is potentially large and could be very attractive to a variety of U. S. suppliers, including the oxygen companies.

<u>Ironmaking</u>. Many steel industry analysts have expressed concern about the future availability of coke. William T. Hogan, S.J.[26] has stated that "There is a strong possibility that by the mid to late 1990's, coke will be in short supply because many coke-oven batteries due for replacement or major repair have not been scheduled for rebuilds. This possibility exists despite the adoption of coal injection and the successful development of alternative methods of making iron."

Acceptance of the AISI smelting reduction process will mainly depend on achieving operating cost advantages and low specific investment costs. Hot metal will have to compete with DRI, which can be applied to EAF steel production. The experience gained from waste oxide recycling should advance the smelting process as a steel plant hot metal producer, both for BOF and EAF steel production.

It seems likely that, by 2005, up to ten smelting plants with an average capacity of 0.7 million net tons per year (0.6 million metric tons per year) could be built in North America to replace coke oven/blast furnace capacity and to meet increased demand for virgin iron units.

The potential for simply applying the AISI/DOE smelting technology to the highly profitable recycling and resource recovery of steel plant waste oxides provides ample justification for a demonstration plant proposal, in terms of both economic and environmental incentives. The very real possibility that this will pave the way for smelting to also become the preferred technology for future replacement of coke ovens and blast furnaces argues strongly for rapid collaborative action by AISI and DOE.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

A five-year, $60 million AISI/DOE program resulted in the development of a technically sound, economically favorable, and environmentally beneficial ironmaking process as a replacement for the coke oven/blast furnace ironmaking process. This one-year, $8 million AISI/DOE Steel Plant Waste Oxide Recycling Program has adapted the process to the recycling of steel plant waste oxides with the following technical, economic, and environmental advantages:

Technical

- Capable of processing all steel plant waste oxides, including dusts, sludges, and oily mill scale, by injection or agglomeration. Dusts containing high levels of zinc can be processed with the reclamation of a zinc-rich sludge for processing by zinc producers.

- Capable of using a wide variety of coals or coke breeze as a fuel.

- Capable of operating as a pressurized, closed system under good process control with easy startup, shutdown, and recovery from outages. It is a forgiving and user-friendly process.

- Capable of thermally-efficient operation with a unique, durable, low-cost water-cooled refractory system. Energy savings of 15 - 25% per ton of hot metal compared to coke oven/blast furnace hot metal.

- Capable of simple casting and desulfurization to produce a blast-furnace-quality hot metal.

Economics

- Operating profits of close to $40 million/year are projected for a $70 million investment when credits for all products (hot metal, zinc sludge, slag, and fuel offgas) and cost avoidance for landfills are taken.

Environment

- Waste materials, currently landfilled, are converted to hot metal and other products, all useful, in an environmentally correct process.

RECOMMENDATIONS

AISI and DOE should make every effort to maintain the momentum of this successful program and push for the construction of a demonstration plant domestically or abroad. AISI will be pleased to work energetically and constructively with any company or consortium to build such a demonstration plant.

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