Magnesium Melt Protection with SO_2 at Meridian Recycling Operations

Meridian - Global Technology Centre

Meridian Technologies Inc.

Outline

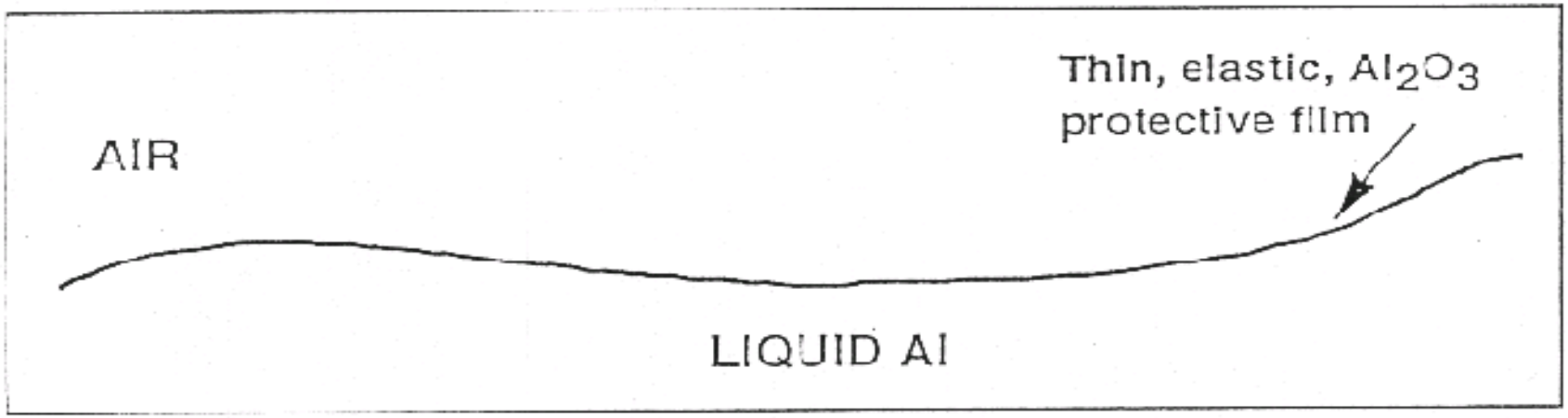
- ✓ Background of Mg melt protection
- ✓ Implementation at Meridian Recycling Operation
- ✓ Testing Results
- ✓ Conclusion

Background - Mg Melt Protection

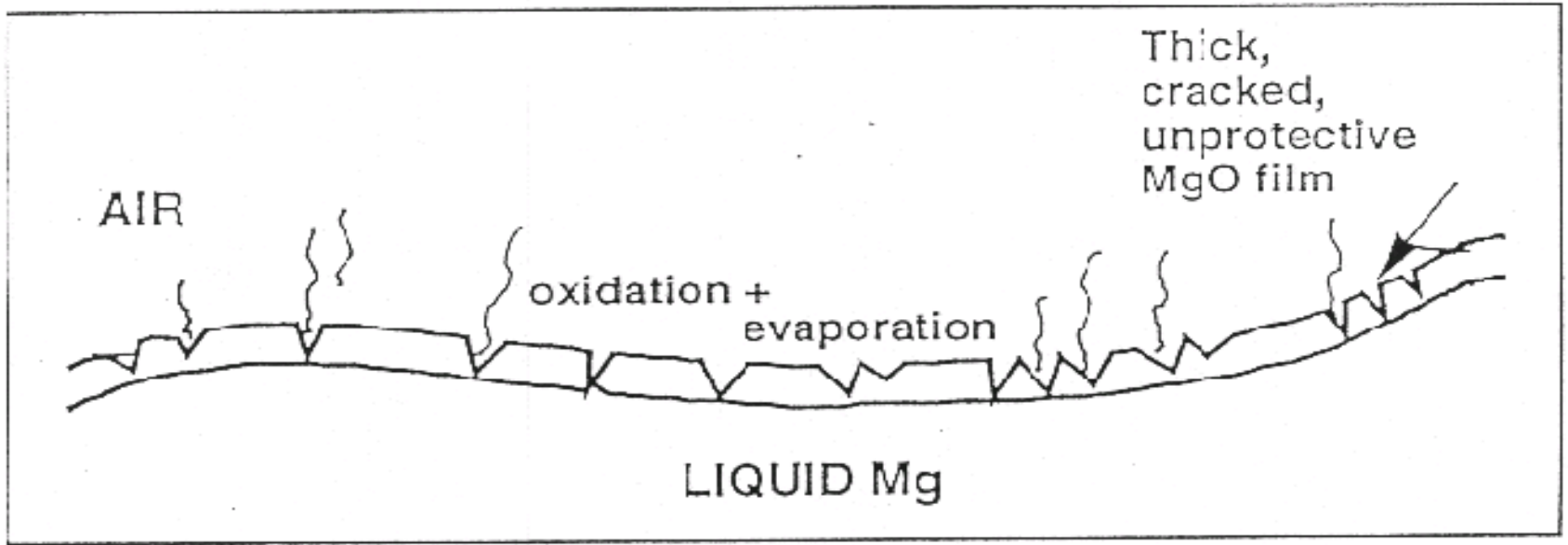
- ✓ Mg melt will burn without protection

- High vapor pressure (361 Pa at 649°)
  (Al: 2.42 x 10^{-06} Pa at 660.25°C)
- The Mg oxide layer is not dense

Background - Mg Melt Protection



(Exothermic = Accelerate reaction)



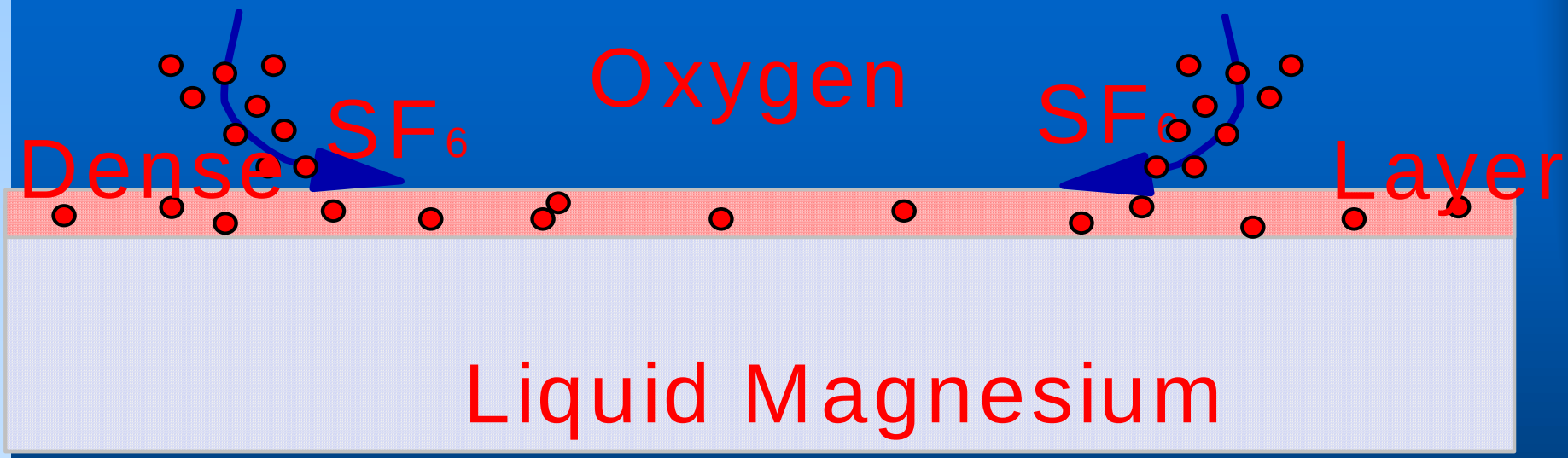
Background - Mg Melt Protection

- ✓ Isolate Mg melt from reacting with oxygen
- Initially Mg industry relied on fluxes as melt protection
  - ⌫ Drawback: entrained salt particles impair corrosion property
- Use of inert gases like argon was early suggested
  - ⌫ Drawback: can not provide good enough protection
- In late 1920's gases forming protective films identified
  - → A U.S. patent from 1934 cited some of these gases among them SF_6, BF_3 and SO_2

Background - Mg Melt Protection

- ✓ SO_2 was first used in Mg industry
  - A dense solid layer of oxide and sulphate/sulphide will form on the top of the melt
  - Effective
  - Drawback: toxic, acidic precipitation
- ✓ In 60's-70's, SF_6 was gradually used
  - A dense solid layer of oxide and fluoride will form on the top of the melt
  - Effective, odorless, Non-toxic
  - Drawback: high GWP (23900, life-time: 3200)

Mechanisms - Mg Melt Protection



Mechanisms - Mg Melt Protection

$$Mg(l) + SO_2(g) + O_2(g) \longrightarrow MgSO_4(s)$$

$$MgSO_4(s) + Mg(l) \longrightarrow MgO(s) + MgS(s)$$

$$Mg(l) + SF_6(g) + O_2(g) \longrightarrow MgO(s) + MgF_2(s) + SO_2F_2(g)$$

The reaction products form a protective layer on the melt

Replacement of SF_6

- ✓ Potential candidates have been identified
  - HFE 7100: C4F9OCH3 (GWP: 390, life-time: 5.0) **(Cleaning solvent and heat transfer fluid)**
  - HFE 7200: C4F9OC2H5 (GWP: 55, life-time: 0.77) **(Cleaning solvent)**
  - HFC 134a: CH2FCF3 (GWP: 1300, life-time: 13.8) **(Refrigerant blend component)**
  - L15566 (3M F-ketone)
  - BF3
- ✓ Intensive research is continuing

Why Converting from SF_6 to SO_2?

- The global warning potential (GWP) of SF_6 is 23,900, life time: 3200 years
- SO_2 has negligible GWP
- SO_2 is the most “realistic” alternative to SF_6 in a short term perspective

Reference Results

- ✓ It has been demonstrated that SO_2 can be successfully used to protect Mg melt both during die casting and ingot casting operations
- ✓ No adverse effects on melt cleanliness and chemistry were observed when Mg melt was protected by SO_2 gas
- ✓ Emission level of SO_2 in the foundry was well below the OSHA limit (2 ppm for 8 hours exposure)
- ✓ Conversion from SF_6 to SO_2 as a protection gas will not degrade quality of recycled ingots

Implementation at Meridian Recycling Operation

Summary of SO_2 H & S

- ✓ Meridian has gone to great lengths to ensure all H,S & E issues have been addressed. We have dealt with M.O.L.,M.O.E.,TSSA, local municipal Gov't and an outside Engineering firm for a PSR . We will be in compliance in all aspects.
- ✓ Training Taken-SCBA, Safe Handling of SO2, Detector, Health Effects, Multi-Gas Vapour Respirator , Mixer Panel and all procedures and instructions.
- ✓ The mixer unit is designed to protect the operators through a complex design of safety features with PLC controls.

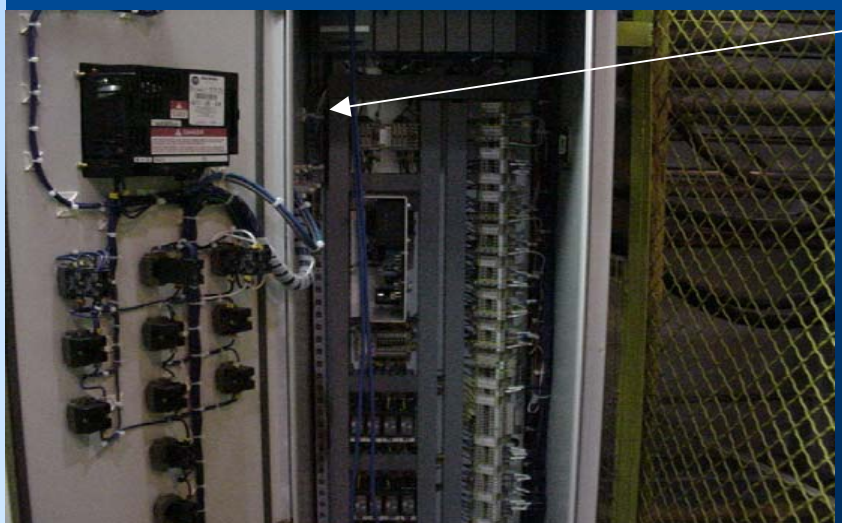
SO_2 Detectors (ppm)

Personal Detector worn by all operators.

Fixed Detectors that are throughout the building. (7)

Mixer Panel

SO_2/Dry Air mix control panel.

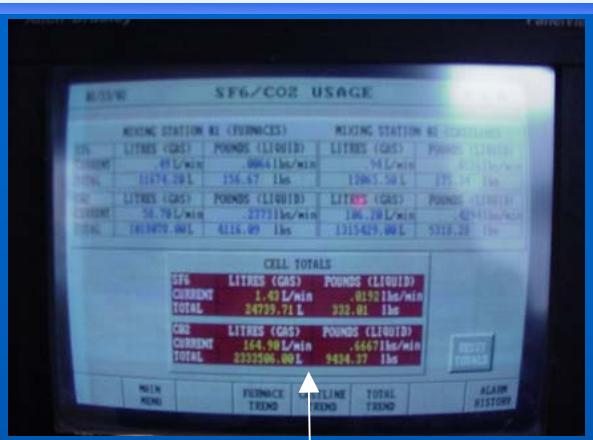


SO_2/Dry Air PLC and controls.

Auxiliary Components

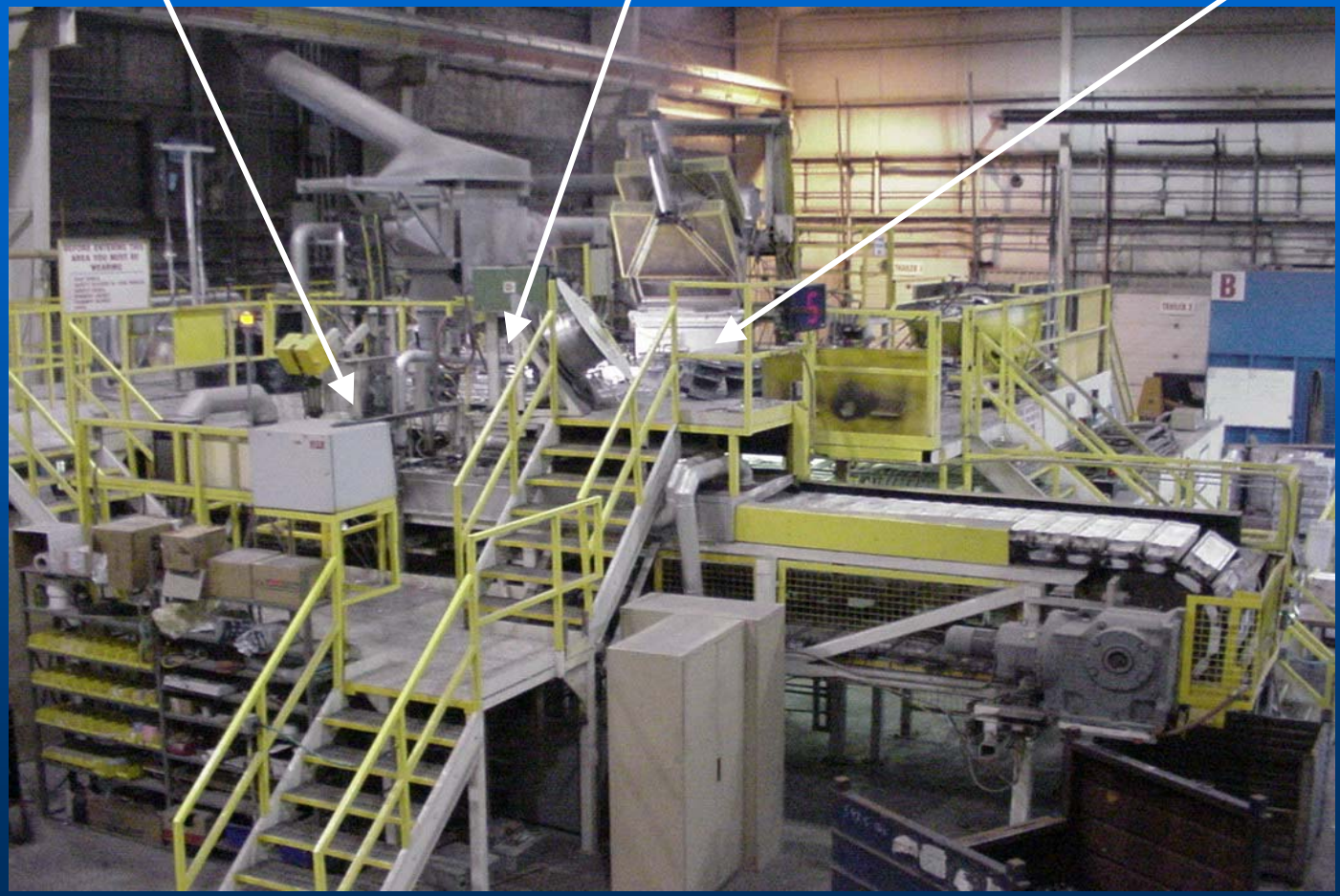
Remote Panel to view all detectors and status of mixer panel.

Auto Switch-over valves. Changes to alternative gas if ppm levels get over pre-determined levels.



Gas Usage Tracking to monitor quantity of gas being supplied. This is a process tool.

Cell Overview – SO_2 Points o f Use



Implementation Timeline

- ✓ SO_2 system was implemented at Meridian recycling plants (Canada) in February 2002.
- Run SO_2 on Refine Furnace (February 2002)
- Run SO_2 on Melt Furnace and Refine Furnace (March 2002)
- Run SO_2 on All locations (April 2002)
- Review all data and make necessary changes (May)

Testing Timeline

✓On-line testing conducted

Test	Visual analysis on ingot surface	Ingot shearing	Chemistry
Frequency	1 ingot/hour	1 ingot/hour	1 sample/2 hours

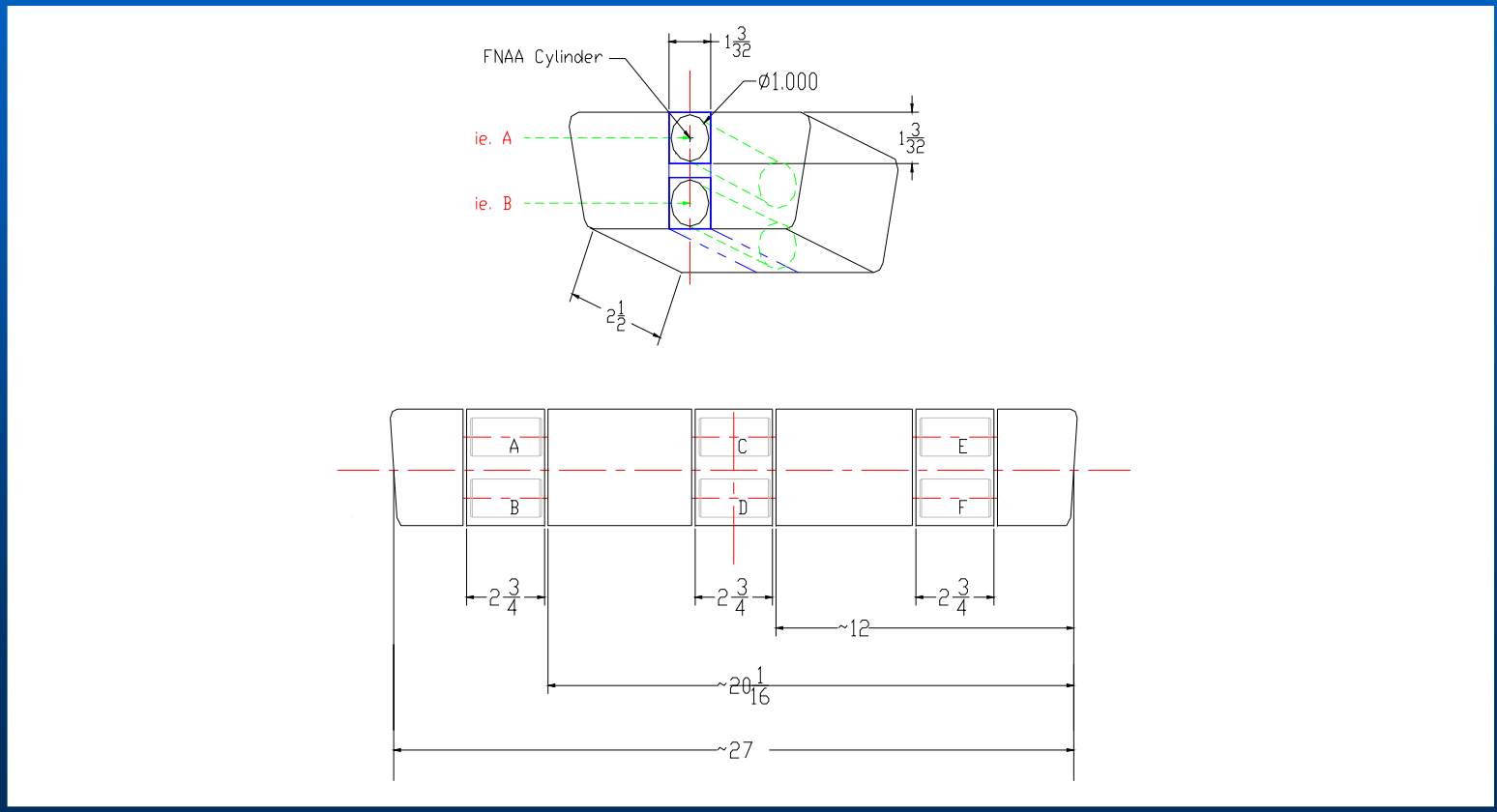
Testing Timeline

- ✓Further test on metal cleanliness for 10 days (April 1 to 10, 2002)

Testing	Time Table	Time Table
FNAA (Texas A&M University)	1 ingot/day for 10 days	10 samples/ingot according to GMW3035 60 samples in total

FNAA Testing for Oxygen

- ✓Six samples/ingot were taken according to GMW3035



Results - FNAA

- ✓10 ingots (April 1 – April 10)

Ingot	A	B	C	D	E	F	average	weighted average
1	51	50	141	50	52	50	65.7	32.8
2	50	50	841	50	55	50	182.7	91.3
3	66	50	142	52	56	50	69.3	34.7
4	50	50	299	50	71	50	95.0	47.5
5	60	50	290	50	50	50	91.7	45.8
6	50	50	57	62	50	50	53.2	26.6
7	59	50	125	50	50	50	64.0	32.0
8	62	50	50	50	50	50	52.0	26.0
9	50	50	657	50	50	50	151.2	75.6
10	50	50	544	50	50	50	132.3	66.2

GM request:

Weighted average<300 ppm

Improvement – Summary on FNAA

- ✓ 10 ingots (April 1 – April 10)

- Metal cleanliness qualified according to GM standard;
- Slightly high oxygen contents in Location C.

Results – FNAA after improvement

- ✓ Improvement was made on casting line
- ✓ 5 ingots (June)

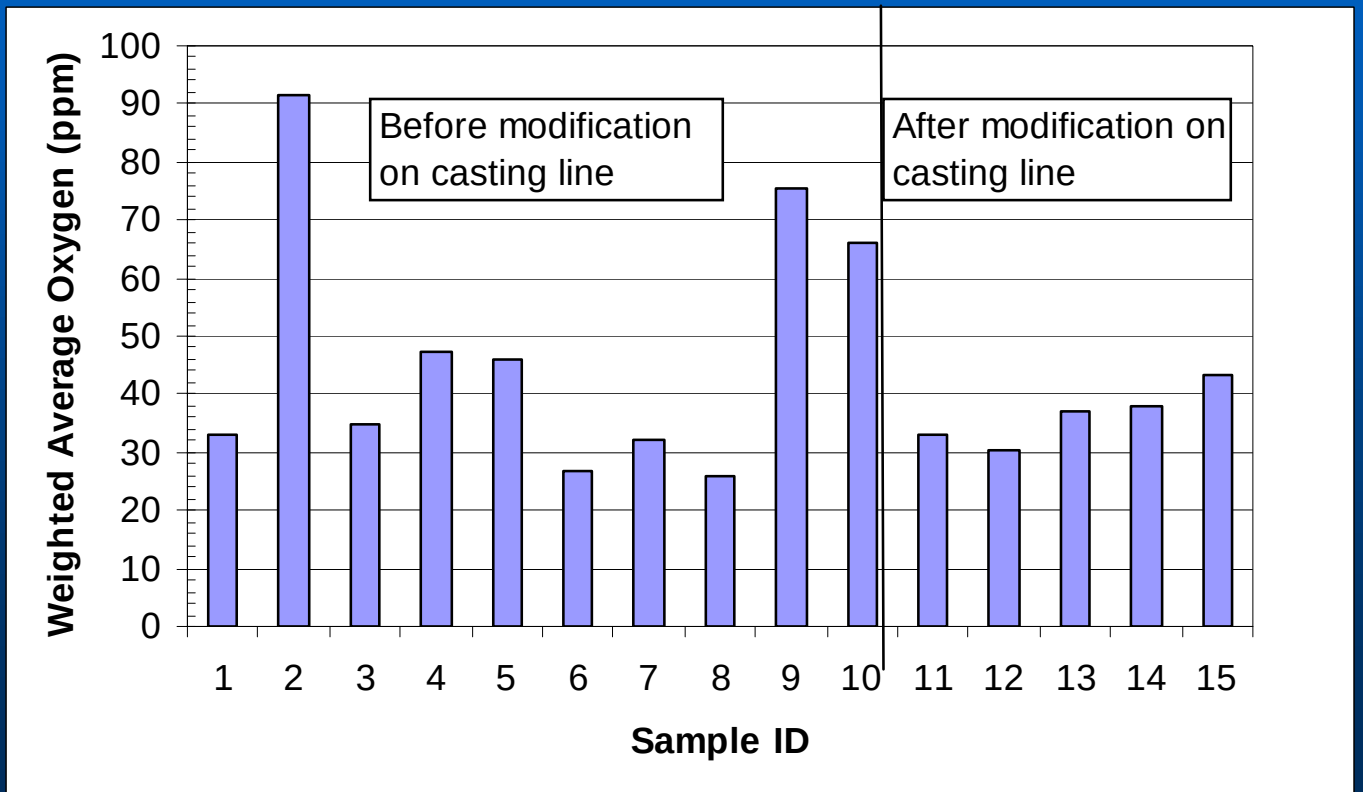
Ingot	A	B	C	D	E	F	average	weighted average
11	50	63	50	145	51	90	65.71	32.86
12	50	102	50	74	50	86	60.57	30.29
13	50	N/A	N/A	181	N/A	51	73.75	36.88
14	50	86	50	169	50	113	76.00	38.00
15	70	101	N/A	133	74	128	86.83	43.42
N/A: invalid sample dimension								

GM request:

Weighted average<300 ppm

Results – FNAA after improvement

- ✓ Improvement on casting line resulted higher cleanliness especially at Location C.



GM request:

Weighted average<300 ppm

Financial Savings

S02 and Dry Air operating costs- approximately range 4 to 10 times less *than other gases studied.*

***Note:** This is estimated for operation only.*
This does not include capital costs for equipment.
Capital for S02 will be slightly higher due to ventilation and S02 detection.

Conclusion

- ✓ SO_2 cover gas has been successfully implemented in Meridian recycling operations (MPD).
- ✓ Metal cleanliness protected by SO_2 is similar to that by SF_6, and qualified to customer standard.
- ✓ SO_2 emission level and safety issues have been handled well in Meridian operations.