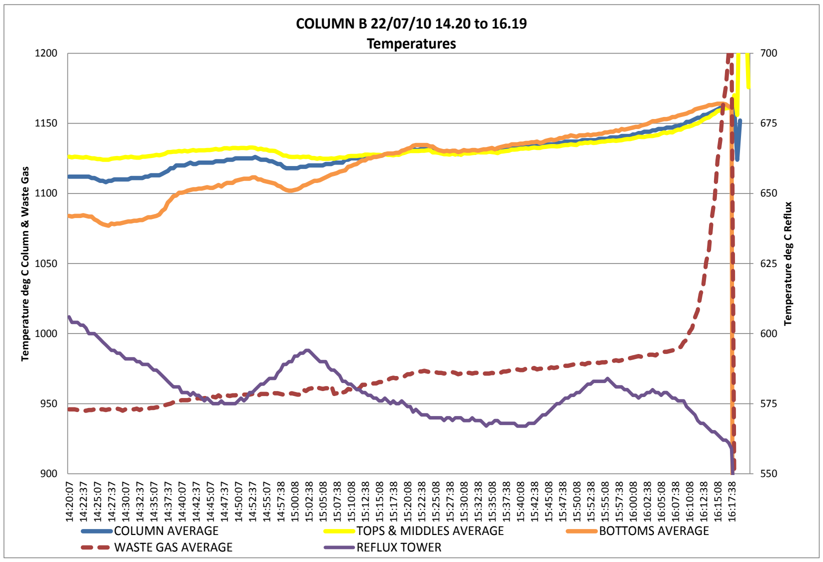
ANALYSIS OF HORSEHEAD CORPORATION MONACA REFINERY FATAL EXPLOSION AND FIRE



JULY 22, 2010

Prepared for the US Chemical Safety Board (CSB)

By William H Hunter MA MIMMM CEng.
Metallurgical Consultant.

Final - 9 March 2015 – Bristol UK

References are provided in Section VIII and marked [Ref:…] in the text.

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ABSTRACT

Horsehead Corporation operated a zinc smelter using secondary (i.e. recycled) materials at Monaca, PA. Part of the metallic crude zinc was refined using the New Jersey distillation process. Distillation columns are each constructed from around 48-60 silicon carbide trays stacked one above the other to a height of some 40 ft (13 m) using mortar joints between trays. The bottom half was heated and the top half allowed fractionation before vapour exit and further processing. The column internals were sealed from the outside using liquid zinc seals.

In the initial stage of the distillation process cadmium was removed in "cadmium" columns. The zinc flowing from the bottom was now free of cadmium but still contained lead and iron impurities. This zinc was then processed in "zinc oxide" columns, where refined zinc was recovered from the column top and was burnt to a zinc oxide product, the remaining impurities being removed in the column bottom product for further processing.

This investigation and analysis shows that the sump at the bottom of the column partially blocked, allowing liquid zinc to "back-fill," flooding trays up the column. This caused the column to act like a pressure cooker and unstable energy store. With a specific gravity close to 7 the pressure within the liquid zinc would reach one atmosphere at a depth of just 1.5 m (7 trays flooded) and the boiling point would rise from 907ºC to 980ºC, with higher figures for increasing numbers of flooded trays. At the same time the high pressure reduced the ability of the column to allow vapour to pass upwards as normal and any boiling that did occur would create pressure surges within the flooded trays.

Eventually the tray wall(s) failed, releasing a surge of vapour that blew out the combustion chamber wall, the vapour and liquid zinc igniting and throwing a flame across the workplace. The rapid surge of vapour resulted from the liquid zinc in the column, now being at atmospheric pressure, cooling back to 907ºC in the only way possible, by part of it instantaneously evaporating. This is best described as an "explosive decompression."

In my professional opinion:

- The physical causes of the accident were a sump design with restricted clearance, known to have contributed to previous accidents and a poorly executed column commissioning, allowing the formation of a sticky zinc oxide dross/liquid zinc emulsion that is known to promote blockages. These factors were aggravated by a high and increasing rate of zinc throughput.
- Human factors played a dominant role. The process is not easy to instrument and awareness of what is happening is vital. Key indications of developing problems in the hours before the accident were not observed and acted upon. In short, because of a history of column blockages and explosions at the Monaca facility, hazardous conditions had been "normalised."
- The scenario described above is the only one that is fully consistent with the witness statements, with control system data from the plant, from information from past incidents and from an understanding of zinc and its properties and behaviour.

I. INTRODUCTION

a On 22 July 2010, the Horsehead zinc plant at Monaca suffered a fatal “explosion and fire.” The incident occurred on one of the “New Jersey” zinc refining columns. It was investigated by OSHA and CSB. The refinery was closed, but the remainder of the site remained operational, the electrothermic furnaces (ETFs) producing unrefined Prime Western zinc (PW). In January 2011, it was announced that the plant had restarted operations, following the investment of $15M in rebuilding and safety improvements. In April 2014, it was announced that the complete Monaca smelter had been permanently closed, to be replaced by already-planned new facilities constructed at Mooresboro, NC.

b My first contact with CSB, who requested a review of its evidence collected and draft conclusions, was in September 2014. This brief was further expanded in October 2014 to establish a clear cause for the explosion.

c My qualifications for the task are as follows:

1. Graduate of Cambridge University, UK in Natural Sciences, specialising in Metallurgy.
2. A 30 year career in operational management of zinc smelters, all of which including a zinc refinery similar to that at Monaca. This career commenced as a shift manager on the zinc refinery.
3. A member of the international team to investigate in 1994 the causes of two fatal accidents involving the zinc refinery distillation columns at Noyelles-Godault, France that occurred in July 1993 and January 1994.
4. Involvement as an expert witness in the corporate manslaughter trial of two former directors of Metaleurop, the owner of the Noyelles-Godault smelter.
5. Co-chair of a conference hosted by ISP, UK in late 1994 to share knowledge gained by the French investigation and other experiences amongst other users of the process; this conference included staff from Horsehead-Monaca, who contributed significantly to participants’ knowledge and understanding.
6. 15 years as a freelance consultant whose prime client was Brook Hunt (now owned by Wood McKenzie), being responsible for its global zinc smelter study, covering technical, costs and commercial analysis, which brought me into contact with many operators of the zinc distillation process, including Horsehead Monaca, as did other freelance work for other clients. My last Horsehead Monaca visit was in 2003, but I was involved in other work for Horsehead Corporation up to 2007.
7. Up to retirement in 2010 a UK registered expert witness.

d. This investigation and report has been an independent desk study based on evidence provided by the Chemical Safety Board and from my own records. The evidence includes Horsehead Monaca computer data, drawings and log sheets; CSB internal memos, two CSB expert reports and CSB and OSHA witness interviews; my own copy of the Zinc Refinery Technical Committee report 1994 (relating to two French explosions) and the Meeting on Refinery Safety and Technology 1994 (meeting held in UK to share knowledge following the French explosions); and my personal knowledge and private communications. I did not have the opportunity to visit the Monaca site after the incident.

Had more information been available, for example operating data prior to and information from the previous B column premature shutdown, process control assays, a report on the materials found in the throat and sump of B column, information on zinc metal flow rates to the columns, a full account of the heat-up of column B including the difficulties at the sump and inadequate sump temperatures and an explanation of excessive liquation pot temperatures, the report would have been more complete; the analysis of the events leading to the explosion, however, would not have changed.

e. The final draft of this report was sent to Horsehead Corporation and the employee union (USW) for comment and their responses are included as Appendices IV and V respectively. Horsehead does not offer any evidence to contradict the reported facts and evidence, but some small requested clarifications have been made in this final version; USW comments reinforce the report.

II. ZINC SMELTING OVERVIEW IN RELATION TO FACILITIES AT HORSEHEAD MONACA AT THE TIME OF THE ACCIDENT

II.I ZINC SMELTING

There are two process routes for zinc production, hydrometallurgical (largely conducted in aqueous solution) and pyrometallurgical (largely conducted using high temperature processes generating zinc in liquid form). The hydrometallurgical route is frequently called the electrolytic process. Zinc is a highly reactive metal and, whichever route is used, a large quantity of energy is required.

Process Stages in the Production of Zinc

Process Stage	Electrolytic	Imperial Smelting	Electrothermic	Vertical Retort
Oxidation	Roasting Leaching	Sintering	Roasting *(and/or Sintering)*	Roasting
Refining	Solution Purification	-	-	-
Reduction	Electrolysis	Blast Furnace	Electric Shaft *(or Electric Arc)*	Vertical Retort
Refining	-	Distillation	Distillation	Distillation
Natural Product	Special High Grade (SHG)	Prime Western (PW)	Prime Western (PW)	99.5% "Crude" Zinc
Residue	Leach Residue	Slag	Slag	Retort Residue

Both process routes in general require an oxidation stage (roasting or sintering) to remove the sulphur present in sulphide raw materials, a reduction stage (electrolysis, blast furnace, electrothermic furnace or vertical retort) to reduce the oxide phases to the metallic form, and a refining stage to remove impurities. These stages and their order are shown above.

The refining stage in the electrolytic route precedes reduction because of the sensitivity of electrolysis to the presence of even very small amounts of impurities, whereas it takes place *after* reduction to crude zinc in most pyrometallurgical processes. This means that the natural product of the electrolytic process is Special High Grade (SHG) zinc, which is pure, and the natural product of most pyrometallurgical processes is Prime Western (PW) zinc, which contains some impurities, principally lead. PW is a general term used in particular in the USA for zinc containing a minimum 98.0% zinc.

The Horsehead Monaca smelter used the Electrothermic Process, a pyrometallurgical process requiring a distillation plant for refining. The refinery was also used for zinc oxide production. The plant had seven electrothermic furnaces, of which five or six were normally operating. It was principally the high cost of the Electrothermic Process that resulted in the relocation of smelting facilities to Mooresboro and the closure of Monaca. Mooresboro uses the Electrolytic Process and, initially at least, there are no facilities to produce zinc oxide.

At Monaca, sinter and pea coke were preheated to around 500^{oC} in drums fired with electrothermic furnace off gas, and charged to the electrothermic furnace by means of rotary distributors. Lumpy feed, including metallic drosses, were added direct. An electrothermic furnace is a vertical cylinder, 2-3 m in diameter and 12-14 m high. Two sets of graphite electrodes, typically 300 mm in diameter, protrude through the wall of the furnace, one set being located near the top of the furnace and the other near the bottom. There are 6 to 9 electrodes in each set. Electricity is passed between the two sets of electrodes, the coke acting as the principal conductor. Typically, the power applied to the furnace is in the range 6 to 9 MW giving a furnace production capacity of 45-65 t/d zinc.

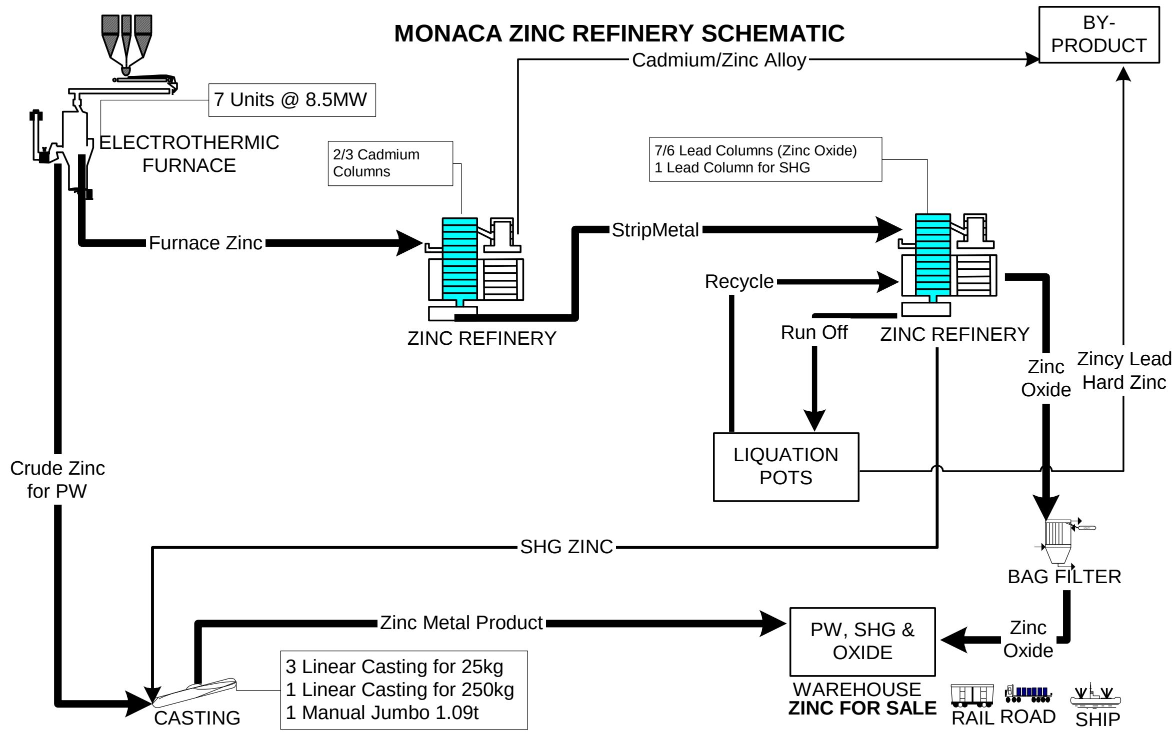
Some 50% of the zinc from the electrothermic furnaces (ETFs) was cast directly to meet Prime Western (PW) quality requirements. The remainder was refined and combusted to zinc oxide, with a small production of SHG.

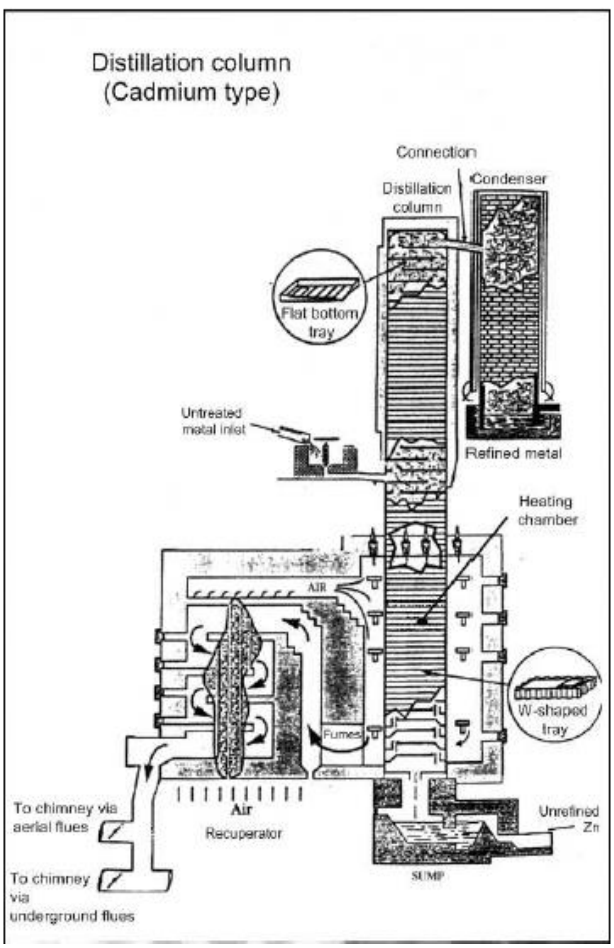
II.II REFINING

Refining of the remaining 50% ETF zinc at Monaca was carried out by the traditional New Jersey distillation method in columns fitted with silicon carbide trays. Heat was provided by a mixture of Low Calorific Value (LCV) gas that was a by-product of the smelting furnaces, and natural gas.

Different plants have different layouts according to the products to be produced and a schematic layout of the Monaca plant is shown in the first figure below.

Distillation columns for zinc refining, whether called “cadmium” or “lead” (generally producing zinc oxide in the case of Monaca) are similar. A cadmium column, similar to those at Monaca, is shown in the second figure below, together with a description.





Source: French Ministry of Environment 2008 – Explosion in a zinc refinery

In a zinc distillation column the lower half of the column, the boiling section, is situated in the combustion or heating chamber and operates at 1,150-1,200ºC. The upper half, the reflux section, is not heated but is insulated to varying degrees and works to rectify and refine the rising vapour. Condensate not making the condenser (i.e. reflux) flows back down to the boiling section. In a lead or zinc oxide column most of the zinc boiled passes to the condenser (or blow-box in the case of a zinc oxide unit), but in a cadmium column most is refluxed to ensure that the condensate reaching the condenser is as rich in cadmium as possible. There are two main types of silicon carbide tray used in a column, boiling or “W” trays in the combustion chamber and “flat” trays in the upper section. Each tray floor has a lip so that it holds some liquid zinc and an orifice (at alternate ends in adjacent trays) in the floor that permits zinc to overflow to the next tray down. Rising zinc vapour can also pass unhindered up to the next tray.

The tray design allows liquid/vapour interaction to be maximised, just like on chemical and oil industry rectification columns for separating completely miscible components possessing differing boiling points. The zinc flowing down the column increases in temperature as it moves down, but cannot go above its boiling point (907ºC) so that, once it reaches that, further energy input causes boiling with vapour being released upwards, in increasing quantities as the heat input from the combustion chamber increases. The act of boiling absorbs much energy (the latent heat of vaporisation). The liquid zinc that finally passes to the sump at the bottom will be close to boiling point. A little heat loss will take place in the sump (depending on the rate of flow) whereupon the zinc exits through the seal into the workplace.

At the Monaca facility, first cadmium was stripped out of the furnace zinc in cadmium columns, typically fed at 75-125 st/d, with about 2 st/d of condensate cadmium/zinc alloy being removed, leaving de-cadmiumised furnace zinc (called strip metal) as run-off. This strip metal then passed to zinc oxide columns (often called lead columns), where the zinc vapour was burnt to zinc oxide in “blow-boxes” – basically boxes with a big zinc fire raging. Often one lead column was reserved at Monaca for making SHG zinc. The run-off zinc – the volume being one quarter to one fifth of the run-off on cadmium columns was liquated (cooled) to a target maximum 450^{oC} in liquation pots (one per column) to drop out a substantial proportion of the heavy impurities (as explained below) and it was then fed back around to the feed of the zinc oxide columns (augmented by “new” strip metal from the cadmium columns). In effect the recycle of run-off is to make up for the feed that did not end up going to the blow-box.

Just by cooling of the run-off, lead separates from the zinc to about 1% and is tapped separately (called zincy lead because it is mainly lead with a small amount of dissolved zinc) from the liquation pot and other impurities are skimmed from the interface between the lead and the cooled zinc. This product is called hard zinc – often called “bottom dross” by galvanisers and “Fe dross” at Monaca. Hard zinc is heavier than zinc.

Whilst the column that exploded at Monaca in 2010 was a cadmium column and hard zinc formation is more likely to occur on lead (zinc oxide) columns, it is appropriate to examine the formation of hard zinc in more detail. Many previous incidents at Monaca had been on the latter type and the cadmium column that exploded had been operating as a zinc oxide column in its previous campaign. The solubility of iron in zinc is shown for various temperatures in the table below, 419ºC being zinc’s freezing point. The changing solubility with temperature is used to separate iron as hard zinc; but it also can create problems if hot liquid zinc containing high levels of dissolved iron cools down and deposits hard zinc in an undesired location, such as inside a column sump.

Temperature $^{\circ}$C	419	450	460	480	500	550	580
Solubility % Fe	0.02	0.035	0.04	0.07	0.1	0.3	0.5

Hard zinc has a typical chemical formula of $FeZn_{13}$, and assays 3-4 % iron (Fe) with the remainder zinc (Zn). One unit of iron takes with it between 25 and 40 units of zinc by weight. Thus a small amount of iron makes a large amount of hard zinc, which is a viscous semi-solid, except when it freezes when it is like concrete - hence the term (hard) zinc.

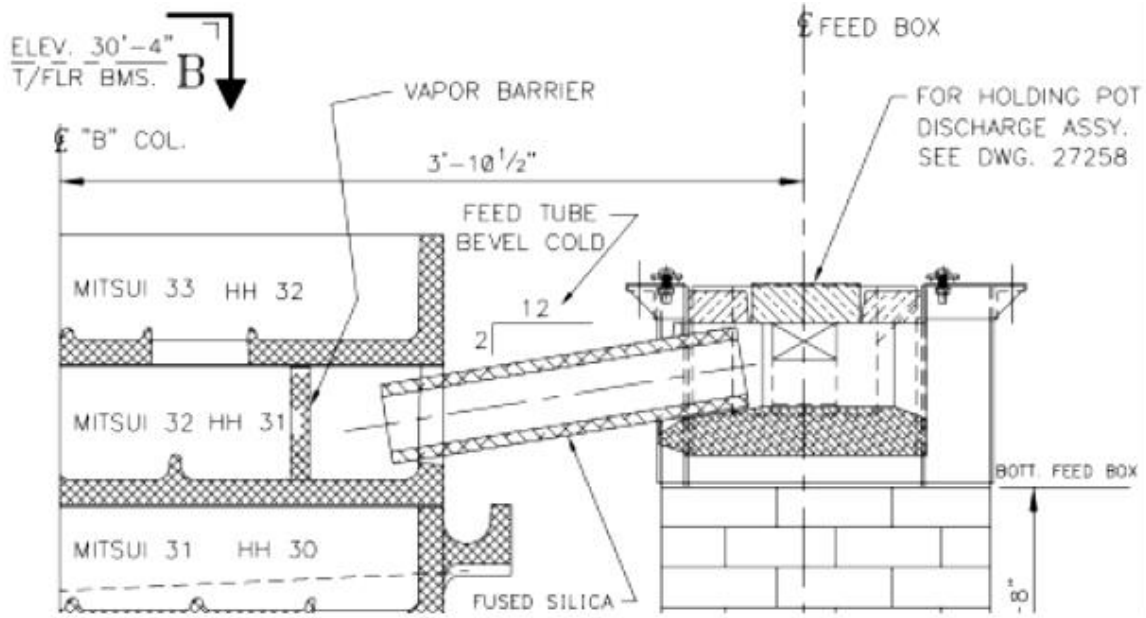
In the passage of zinc through a column, the iron will all pass to the run-off and its concentration will therefore increase in the ratio of feed rate to run-off rate. Of course the run-off will exit the column at a reasonably high temperature, but there can still be a risk that it may be low enough to precipitate out hard zinc. If, for example, the feed to a lead (zinc oxide) column is 60 t/d and is saturated with iron at its last liquation (say 0.03% Fe), and if the run-off is 25 t/d, the composition of the run-off recycle will be 0.072% Fe. This level should be acceptable but iron could quite easily precipitate as hard zinc before it exits the column sump if the temperature is not high enough or if the feed rate drops off. This might then cause an obstruction in the sump. The column operating regime should be set to avoid this.

If, for example, the liquation pot was being operated at an excessive 550ºC, the run-off recycle would contain 0.3% Fe. The subsequent run-off could then, with the "new" iron from new strip metal, contain 0.34% Fe. The sump temperature could now *easily* be low enough to allow clogging with hard metal.

Lead will also concentrate and come out of solution on cooling, but is less likely to be a problem since it is compact and remains liquid down to 327ºC. At zinc's melting point, 419ºC, the solubility of lead in zinc is 0.9% and at 450 ºC it is 1.4%.

A column is designed to be air tight, having liquid zinc metal seals at its three orifices, feed box, sump (and condenser sump on a lead or cadmium column). These consist of an underflow/overflow, like a drain trap, and would have a seal of around 3-4 inches (75-100 mm) of liquid zinc. The seal at the Monaca column sumps was $3^{7}/_{8}$ inches. Liquid zinc has a specific gravity of 6.57 at its melting point and a little lower at higher temperatures. Since the column operates internally at low pressure, this seal would require an internal pressure of just 0.066 bar (atmosphere) or 25 inches water gauge to blow it. This would only happen in *extreme* circumstances, because the normal internal pressure is still lower.

The most problematical seal is at the feedbox, shown below at Horsehead Monaca (from Horsehead drawing #26046-12). It relies on a good seal on the feedbox cover tile. If heating input or feed rate varies the column, until it settles out under the new regime, will undergo internal pressure or suction changes (the former for lower feed/higher heat input and the latter for the reverse). Under suction, which is hard to detect, air may be drawn in if the cover tile seal is not absolutely perfect. Any leakage here renders the liquid metal seal ineffective, and air ingress will be a cause of dross (zinc oxide) formation, and moisture in the air can make the dross sticky; ultimately any dross formed must be able to exit the sump. Steady feed and firing minimises such disturbances.



One important clearance in the sump to avoid blockages is the minimum vertical depth below the underflow and is, at most plants, 130-180 mm ("two bricks" or more). The depth is not only important to allow passage of zinc and associated debris (dross, little bits of brick and mortar) but the act of sweeping the sump clear (called "strapping" by Horsehead) is like carrying out keyhole surgery at the end of a 3.5 m long bendy bar. In this case it is without a camera and it is easy to miss the underflow.

As mentioned, the boiling trays are shaped as an elongated W, meaning that there is a deep channel around the perimeter in order to increase the surface area of liquid zinc in contact with the wall, since heat transfer from the combustion chamber to the zinc in the boiling zone can only occur through the side walls. As it takes four to six hours on column commissioning for feed metal, at say 30t/h, to reach the sump, it follows that the column contains some four to seven tonnes of molten zinc (as working inventory) when operating normally.

A column in which zinc is refined by distillation has a finite life. The life is dependent on a number of factors, including the quality of the silicon carbide trays from which it was constructed, how smoothly it has been operated (to avoid thermal stress) and the level of iron impurity in the zinc being refined (because this can react with silicon carbide, particularly as its concentration increases in the lower trays). Typically the life of a column will be between 24 and 48 months. Silicon carbide, whilst physically strong, suffers damage from thermal shock and, as an example of the care required, commissioning of a column can take around a week, since the heating schedule will often be conducted at a rate as low as 4^{oC} per hour.

Through the life of a column, leaks develop and require patching, using crude brushes and mortar or a slurry blown onto the leak using a blowpipe. Leaks occur usually as a result of unintended thermal stress. Panels of soft bricks, sealed using soft mortar "B-mix", are left in the combustion chamber wall to allow easy access for patching. Since the columns are arranged in a line side by side, and the recuperator, which utilises heat from the waste gases to preheat combustion air, blocks the "rear" wall, the only access is through the "front" wall.

Leakage of zinc from a column is normal and usually increases if it suffers a history of undesirable deviations from steady operations, mainly feed or firing. Leakage from the upper section can be captured at the combustion chamber roof, although some often bypasses collection. The presence of liquid zinc in the combustion chamber, whilst undesirable, is not abnormal and, in the above circumstances, is a benign nuisance. It does not cause explosions. The zinc burns to zinc oxide and, over time, it blocks exit ports and the recuperator, which require cleaning (Horsehead employees call it “Column Work”). Burning liquid zinc tends to cover itself with a layer of oxide which makes the zinc surface less available to any air for further combustion and zinc oxide is only commercially produced thermally from vapour form.

In past times the columns were typically drafted directly to a chimney, the natural draft being sufficient to keep the process going. Few workers on the plant would not glance at the chimneys on their way into work to assess the zinc “plume” and gather a feel of how the day would be. Increasing environmental legislation has meant that bag filters with induced draft ventilation have had to be installed at many plants. This was the case at Monaca. It means that leakage could not so easily be assessed by “a glance at the chimneys.” On the other hand, patching work can continue without concerns over environmental impact.

When a column fails, the heating of the column is turned off, as is the feed of zinc. After cooling, the column is demolished and then rebuilt using a fresh supply of silicon carbide trays. Mortar is used to seal the joints with the trays above and below. Since it is difficult to clean off “squeezed out” mortar from the internals of each tray (the only cleaning access is downwards through the vapour hole at one end), inevitably there will be left some small pieces of debris, which the column must be able to tolerate in operation without blocking at the sump. Monaca aims for a joint thickness of 1/8 inch [Ref: Int. 1]; this is thicker than at many plants, the German smelter reporting [Ref: 9, p. 18] just 0-1.5 mm (0-1/16 inch).

In my professional opinion the thin joints and recognition of point contact at the German smelter, is correct and common practice. With the quality of machine grinding achievable, there will be point contact in many places, so that mortar will be present only in small amounts and sufficient only to provide a seal – there is no purpose in having more. Indeed, the worry with a thick joint would be that significant internal pressure could “blow” it. A nominal allowance for joints may be made on the assembly drawing, but this is to ensure that, when building the column, the position of the feed tray is such as to ensure that feed could flow down- not up-hill.

Trays are typically laid on the basis of just 7-8 per day [Ref: 9, p. 18], since the entire column is resting solely on the sump, is not supported at the sides and must rise straight up for some 40 feet (13 m). Horsehead Monaca reports around 20/day [Ref: Int. 2]. Following a slow heating procedure the rebuilt column can be brought back into service. Typically the time from “offline” to “online” is four to six weeks.

Operation of a zinc refinery requires steady conditions of feed and firing. The operators controlling the column and its feed, firing, condenser and run-off need to operate a system of “check this, check that, anticipate and clean and poke” in order to stay steady and avoid upsets. Steady operation is a reflection of good design and competent and systematic attention to operating detail.

III SEVERE ACCIDENTS IN ZINC REFINERIES

Zinc refining by New Jersey distillation is a process in which major accidents have occurred, and this was brought to a head at Noyelles-Godault France in 1993 and 1994, when two major "explosions" occurred, resulting in 11 fatalities and many injuries from severe burns. Following the second accident an international team was formed to investigate. On investigation it was found that the same sequence of events must have occurred in up to ten *other* major incidents elsewhere in the world, although at the time it had not been suspected. The cause was found to be a sequence of events starting with a partial blockage of a column sump, followed by back filling of the column with liquid zinc. The submerged boiling, during which the zinc vapour would have difficulty in escaping, caused vibrations and ultimate failure of the tray(s) by fatigue at high pressure. The rapid outflow of zinc vapour and droplets of superheated liquid immediately ignited causing a pressure surge that destroyed the combustion chamber wall and created a major conflagration in the workplace [Ref: 1; 2; 9, p. 5]. Zinc is a highly reactive metal, particularly in vapour form.

An Australian zinc smelter suffered a blocked sump in 1973 [Ref: 1; 9 p. 10]. The foreman went to clear it by "rodding." In this case the blockage was cleared but this action released large quantities of zinc vapour and superheated liquid zinc directly at the foreman, who could not escape and was burned to death. It was calculated that the column was flooded to at least the ninth tray. Once the blockage had been cleared, it was possible for the high column internal pressure to cause the metal seal at the sump to be blown, releasing high pressure zinc vapour and liquid. The sump area is hazardous and the design of the complete column/recuperator structure limits good access and escape routes.

The FYR of Macedonia smelter suffered a similar accident in 1994 [Ref: 9, p. 8] following a sump blockage. On releasing the blockage, 1.5 t of zinc came out which killed the worker. In 1993, an Indian smelter suffered an explosion [Ref: 9, p. 10] that blew out the combustion chamber and killed one operator.

The Horsehead Monaca smelter itself has suffered numerous major incidents, although it was not, from available data, until 2010 when fatalities and major injuries occurred. In December 1993 a lead column exploded [Ref: 9, p. 9]. In July 1994, a badly leaking column was shutdown prematurely due to safety concerns [Ref: Int. 3], and this incident was reported in October 1994 to the UK-hosted conference [Ref: 9, p. 9] to which representatives of Monaca were invited, and attended. It was absolutely clear that the column was at least partially blocked from the sump upwards and that a major accident had been imminent but was fortuitously averted. The fact that, in this case, the column was not destroyed provided useful knowledge to all the conference participants, some of whom had not previously believed that columns could back-fill in this way. In particular, parts of the floor of tray #6 were found in tray #14, and they could only have gotten there by floating up the column, which must therefore have been flooded. Spongy material was found in the sump, from which liquid zinc continuously drained for four hours after shut down as if the feed had not been stopped.

A list of five Horsehead explosions is provided [Ref: 3], many of which have sump blockages as features, two of which were in 1997 and 2007. All were on zinc oxide columns. A Horsehead interview [Ref: Int. 4] recognises the risk of massive loss of molten zinc into the heating chamber.

Other operators of the process have also reported incidents of partial blocking since the French accidents. Although there were a number of Western World pyrometallurgical smelters with zinc distillation refineries up to the early 2000s, many have closed for economic reasons, but China is still a major producer of pyrometallurgical zinc, which is refined by distillation.

This type of incident involving restriction in the sump resulting in backfilling of trays could be named the ***"Pressure Cooker Explosion,"*** having the features:

a. Partial or complete restriction of run-off flow at the sump,
b. A gradual build-up of liquid zinc (backfill) in the column. At this point the chain of events leading to disaster has started, but is recoverable.
c. Backfilling continues until some trays are full of liquid zinc. Liquid zinc is still trying to boil and this, together with pressure surges as vapour tries to escape, will put the walls and floors of the trays under increased internal pressure. Some vibrations may occur. The column is now operating outside its design conditions.
d. Just 1.5 m (liquid zinc has a specific gravity of 6-6.5 depending on temperature) of backfill (just 7.5 trays) will increase the internal hydrostatic pressure at the bottom by one bar (atmosphere). The increased pressure will increase the boiling point of zinc (from 907ºC to 980ºC) [Ref: 4] and create superheated zinc. The zinc boiling point for two bar pressure is 1027ºC. As explained earlier, the internal column temperature in this area will be at this (increased) boiling point of zinc. The column is operating as a pressure cooker. In a kitchen pressure cooker, typically at 1 bar (atmosphere), the boiling point of water increases from 100ºC to 120ºC.
e. The raised boiling point of zinc raises the operating temperature within the column and this is reflected in gradually rising lower combustion chamber and waste gas temperatures. And the pressurised zinc may reduce the production of vapour at the condenser (*vacuum* distillation is used to *enhance* distillation, but under pressure the opposite occurs).
f. Depending on the duration of abnormal conditions and other factors, including the effect of fatigue on the trays, at some point one or more tray walls will fail outwards unless the backfilling condition is reversed, releasing accumulated zinc vapour plus spontaneous "flash" vapour created from the superheated zinc, together with liquid zinc, probably as a spray. All of these will exit at pressure. Total control of the process has now been lost.
g. This zinc release will ignite, and consume free oxygen in the combustion chamber.
h. The combustion chamber wall will explode due to the increased pressure, the explosion panels not taking much over-pressure to blow them out.
i. Zinc vapour and superheated zinc spray exiting from the combustion chamber immediately ignites when it meets workplace air, throwing a flame directly out from the combustion chamber wall causing major damage and injury, often fatal.
j. How much vapour and liquid zinc is released and how big the explosive flame will be depends on how much liquid zinc has backfilled the trays.

In my opinion, *a **"Pressure Cooker Explosion"*** constitutes the major life-threatening hazard of the New Jersey process, since vapour from boiling is not able to take the normal easy way out, up the column and away. Risk management has to be directed at preventing sump restrictions and identifying those that do occur early enough to take remedial action. The principal steps for achieving this are as follows:

- Best practice standards of management.
- Best practice standards of training and awareness and good operator plant information systems.

- Taking all possible steps to prevent the ingress of air to the column – i.e. at the feed point, at the condenser and at the sump. Air plus zinc makes zinc oxide; zinc oxide is a solid and can contribute to blockages and, if coated on an internal wall, can reduce heat transfer; the 80% of remaining nitrogen in the column can itself cause unstable operation.
- Good dross (zinc oxide) separation at the feedbox. Note that dross floats on zinc, but sometimes "mushy dross" is formed which appears to be fine dross and entrained liquid zinc existing as a combined emulsion layer on top of the liquid zinc [Ref: 2].
- Constant checking that the column sump is running normally, i.e. preventing any possible accumulation of liquid zinc in the column.
- Design clearances that are adequate to allow the passage of inevitable small amounts of solids with the zinc.
- An avoidance of too low a "run-off" operating regime, in order that any solids such as zinc-iron compounds (hard zinc) are preferably not formed, but if they are, can be easily flushed away.

This is the background to the assessment of the 22 July 2010 Fatal Accident and Fire at Horsehead Monaca.

IV DISCUSSION OF WHAT HAPPENED AT HORSEHEAD MONACA ON 22 JULY 2010

IV.I EXAMINATION OF DATA

An aerial view of the Horsehead Monaca facility is shown below, with the red box outlining the refinery building.

This photograph shows a typical scene within the plant after the explosion and fire. It is a general view showing damaged plant and equipment, all covered with a zinc oxide ash.

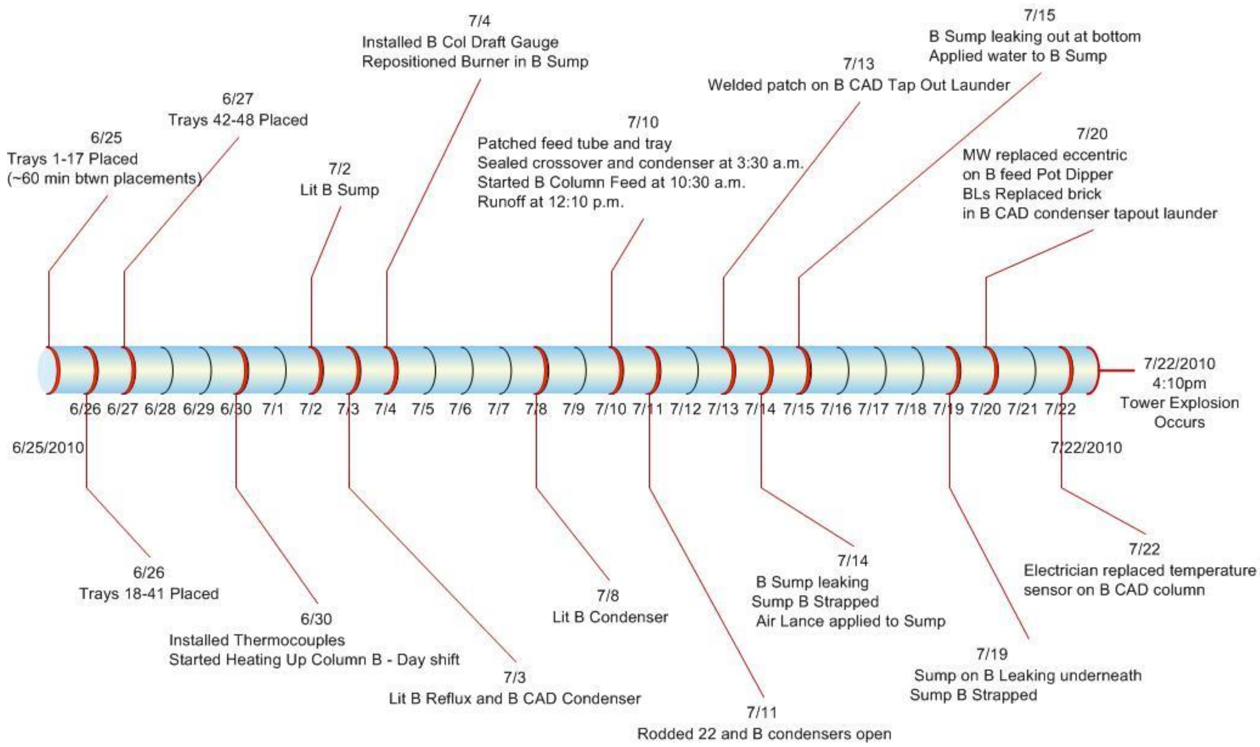
The general photographs of the plant are similar to the scene at Noyelles-Godault France after the 1994 explosion at that plant. Bricks were blown everywhere and there was damage to steelwork, but the building structure and much of the equipment was largely intact.

This photograph shows the combustion chamber wall of column B, and the site of the explosion, the pressure relief panels being blown out into the workplace.

This photograph shows the reflux tower after the explosion. The trays in the combustion chamber have collapsed but the reflux tower is largely undamaged, having dropped a few feet such that the framework for the reflux section insulation was sitting on the combustion chamber roof.

IV.I.I The Timeline

The headline report of the explosion concentrates on the 10 minutes between the first alarm for temperature rate of change and the explosion. These incidents generally have a much longer timescale and the column timeline from warm up to the explosion is shown below [Ref: 5].



Horsehead Corporation B Column Timeline
June 25, 2010 – July 22, 2010

July 22, 2010, 4:10pm, Tower Explosion Occurs

The most important facts are as follows:

- Although the timeline shows the sump burner being lit on 2 July, the Column Heat-Up log [Ref: 6 and shown in Appendix I] shows the sump temperature well below target; this continued right through the warm-up with the highest temperature recorded being 380ºC on 6 July; temperatures well below the target of 650ºC continued for the last few days before feed. The sump burner is the means to warm the column from the *inside* and to dry any mortar in the sump or under tray #1.
- Witness interviews referred to bricklayers "working in the sump" and to the sump burner not being present [Ref: Int. 5]. One of the operators referred specifically to the fact that the sump burner flame (when the burner was present) was not being pulled into the sump, even with the cover tiles off, and thought that there was a problem with the sump.
- Column feed was put to the column on 10 July (and the log sheets show the first cadmium-zinc alloy condensate was tapped on 12 July) – perfectly normal.
- The timeline shows B sump leaking (suggesting blockage) being strapped on 14 July and an air

lance being applied to the sump. Leaks occurred again on 15 July. Further strapping took place on 19 July when the sump leaked. Clearly there were continuing problems with the sump. On the basis of the ladle logs, the feed rate to column B was being increased over this period; more feed means more run-off (strip metal) needing to exit the sump.

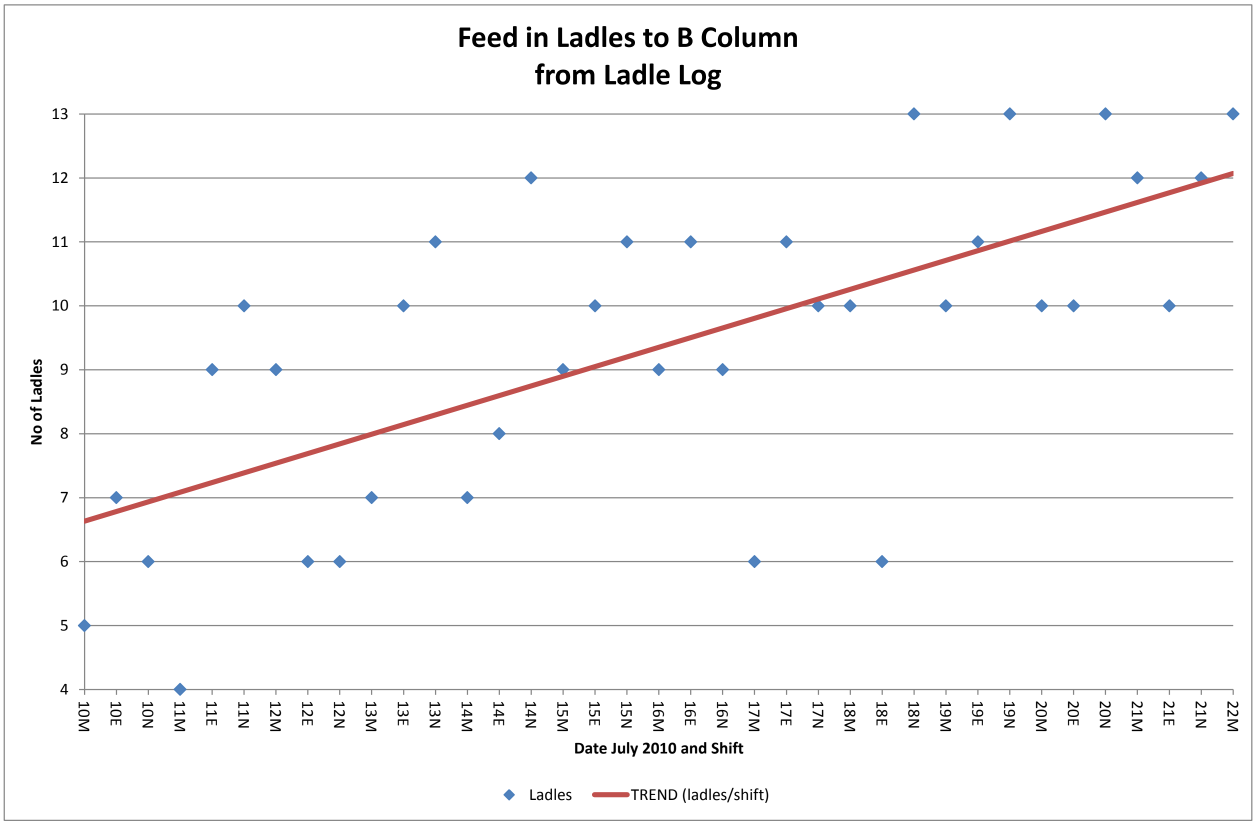
- What is not shown on the timeline was a finding by a feed operator [Ref: Int. 6] of a crack in a tray below the feed tray after feed started. This "neck" area of the column is mainly heated by the hot internal gases emanating from the sump burner – in the absence of this the tray may have cracked due to thermal stress when feed was introduced.
- Sump problems on B column were mentioned in many interviews [Ref: Int. 7].
- Approximately 10 minutes before the explosion there was an alarm indicating a high rate of temperature change covering the column waste gas temperature, and the operator cut the gas input flow. Following a further alarm he cut gas further, and shortly afterwards the column exploded. The operator actions were exactly those required by the procedure [Ref: 7]. The action was to "Item 1 – Waste Gas Temperatures Rapidly Rising." Had it been to "Item 2 – Oxide Combustion Unit (Down Draft), Flickering of Vapour," the procedure would have required the operator to inspect the column through nostril boxes (peepholes next to the column burners) for "dark trays" – a sign of zinc backfilling the column. As a result no one inspected the nostril boxes [Ref: Int. 8]. In my professional opinion it was almost certainly too late to do anything anyway, but I suspect that an inspection would have shown "black trays" and probably intensive zinc combustion. The events leading up to the *previous* B column premature shutdown are described [Ref: Int. 8], and show that the column clearly backed up. Showing through the nostril boxes were "black trays" and a *"ring of fire."*
- The emergency procedure mentioned above [Ref: 7] clearly associates sump blockages with zinc oxide columns only.
- Prior to the explosion, many workers reported that everything appeared to be normal [Ref: Int. 9].

IV.I.II The Log Sheets

The data from first column feed to the explosion as interpreted from the ladle logs [Ref: 18 and Appendix II (extracts)] are shown below. The Log Sheets for the Refinery [Ref: 12 & 18] do not show inputs to the columns as tonnages, but as number of ladles so that column feed rates have to be estimated. It appears that B column was operating at a feed rate of approximately 110 st/day on the morning of 22 July 2010, an increase from the previous two shifts; strip metal tonnage would be similar but slightly lower.

The chart shows large variations in the number of ladles fed from one shift to another. Although the needle valve before the feed box (Section IV.I.III) will smooth the flow to some extent, it may be that feed variations at Monaca were quite significant. Any variation creates an opportunity for air ingress and the subsequent production of zinc oxide dross.

Oxide columns appear to have been operated at approximately 60st/day feed, with 34st/d going to oxide production and the remainder being run-off (26 st/day). This shows the major difference between the two types of column.



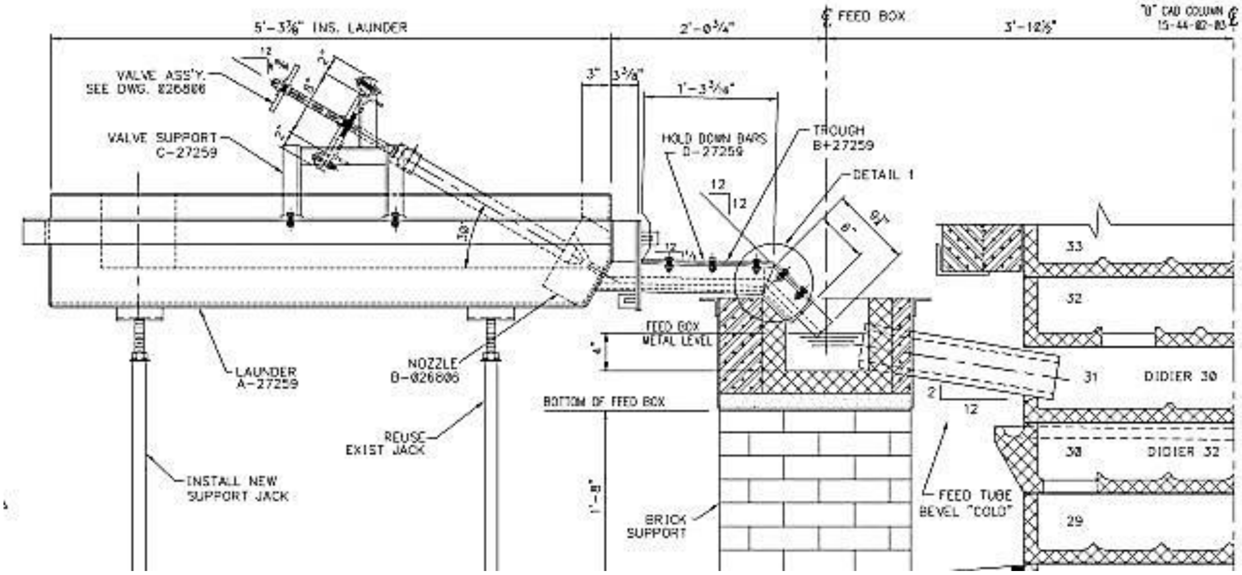
There is little more to learn from these log sheets, other than events listed on the previously discussed timeline. However it is of concern that the logged temperatures for liquation pots are frequently considerably higher than the target of not more than 450ºC. For example, column 25 evening shift shows 550ºC and 530ºC for the night of 21 July 2010 and following morning [See examples in Appendix II]. This indicates that excessive quantities of iron may have been recycling to the oxide column feeds. This would have had no influence on B column but, as a general observation, suggests that the zinc oxide columns would be at risk of hard zinc deposition in the sump.

IV.I.III The Feed Arrangement and Sump on Column B

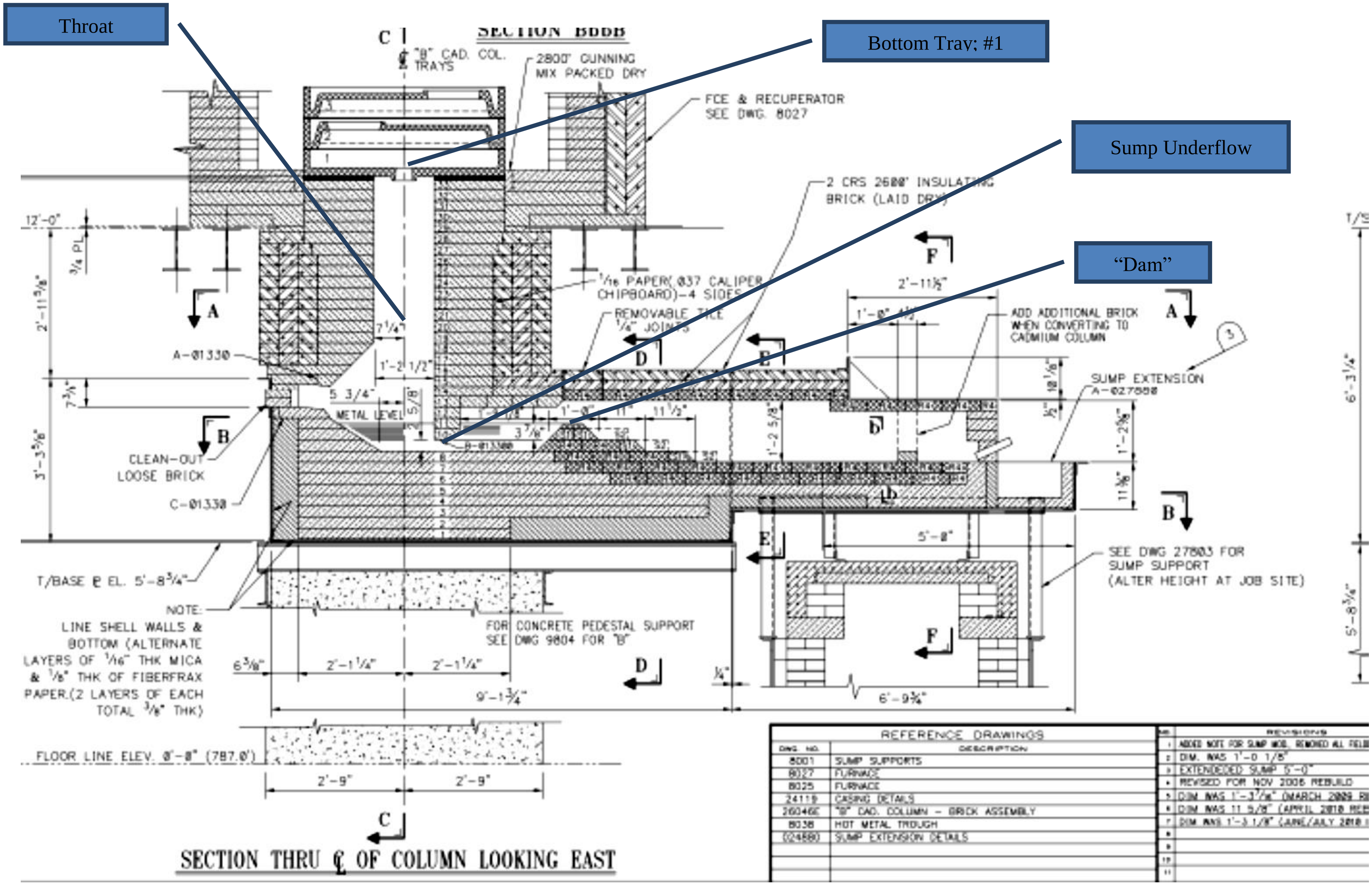
It is worth examining the column feed area, since dross and/or air can be entrained with the feed metal and then cause problems within the column. As explained [Ref: 2], to quote "……..*the phenomenon of liquid zinc forming a viscous foam or paste when it is mixed with zinc oxide. The density of liquid zinc is about 7t/m^3 and that of zinc oxide is about 2.5-3t/m^3. When in contact with air molten zinc of 900º*C *is readily oxidised, and the solid oxide floats as a surface layer on the liquid. When the liquid then drips and trickles down to lower trays and also, in reverse direction, the gas, consisting of air and zinc vapour, bubbles through liquid zinc, the mass gets well stirred. It then starts to become a thick viscous and foamy mass or paste. Laboratory tests have shown the thickening mechanism described above clearly."*

Below is shown the needle valve and launder system to the feed box of column B (from Horsehead drawing #27258 – note that this drawing does not show the feed tray internal baffle). The valve, although at an angle, was "top down" through the valve, allowing dross and air to be more easily drawn down through the needle valve with the liquid zinc. Although the feed box is designed to settle out dross, some dross and air may still be entrained in the liquid zinc flowing to the column. The conclusion from the Noyelles-Godault investigation [Ref: 1, p. 60] was that the flow should be "bottom up."

Although the needle valve will regulate liquid zinc flow, variations in the liquid metal level in the launder will cause the flow rate to vary, albeit not directly in proportion to the metal level. As already explained in Section II.II, variations in feed rate affect the column internal pressure and air can easily be drawn into the column when under suction and then react to form zinc oxide dross.



The drawing below shows the column sump of B column as it was on the B column that exploded [Ref: 8]. The sump underflow and the bottom tray of the column are clearly marked.


Throat
Bottom Tray; #1
Sump Underflow
"Dam"
"B" CAD. COL. TRAYS
2800" GUNNING MIX PACKED DRY
FCE & RECUPERATOR SEE DWG. 8027
2 CRS 2600' INSULATING BRICK (LAID DRY)
1/16 PAPER(.037 CALIPER CHIPBOARD)-4 SIDES
REMOVABLE TILE 1/4" JOINTS
ADD ADDITIONAL BRICK WHEN CONVERTING TO CADMIUM COLUMN
SUMP EXTENSION
METAL LEVEL
CLEAN-OUT LOOSE BRICK
T/BASE PL EL. 5'-8 3/4"
NOTE:
LINE SHELL WALLS & BOTTOM (ALTERNATE LAYERS OF 1/16" THK MICA & 1/8" THK OF FIBERFRAX PAPER.(2 LAYERS OF EACH TOTAL 3/8" THK)
FOR CONCRETE PEDESTAL SUPPORT SEE DWG 9804 FOR "B"
SEE DWG 27803 FOR SUMP SUPPORT (ALTER HEIGHT AT JOB SITE)
FLOOR LINE ELEV. 0'-0" (787.0')
SECTION THRU ℄ OF COLUMN LOOKING EAST
REFERENCE DRAWINGS
8001 SUMP SUPPORTS
8027 FURNACE
8025 FURNACE
24119 CASING DETAILS
26046E "B" CAD. COLUMN - BRICK ASSEMBLY
8038 HOT METAL TROUGH
024880 SUMP EXTENSION DETAILS
REVISIONS

Above the sump can be seen the first two boiling (W) trays. It is worth noting the distance of the underflow to the external point on the sump of some 150 inches (3.8 m). This is what must be traversed by a rod or strap worked remotely by an operator, or as described by an operator [Ref: Int. 10] *"No one has X-ray vision."* It is therefore a skilled task to find and clear the underflow slot.

One important dimension is the clearance under the underflow, the point of greatest restriction to the passage of zinc, dross and any debris. The dimension is shown as $2^{5}/_{8}$ inches ("1 brick"), about 65 mm. This was far less than most, if not all, zinc refineries. Many plants increased the dimension to "2 bricks" after the Australian fatality in 1973. The Noyelles-Godault accidents [Ref: 1, p. 32] were both on columns with 70mm - "1 brick" underflows [Ref: 9, p. 14], the explosions were both on cadmium columns and the company had only carried out the change (up to these accidents) to "2 bricks" on lead and reboiler columns. Most other plants still at "1 brick" changed to "2 bricks" following a conference at Bristol UK in late 1994 [Ref: 9].

After the explosion and the dismantling of the column, it was possible to examine what was found in and around the sump. The photograph below of tray #1 (underside) apparently shows a plug of material blocking the drain hole with stalactites underneath and the description on the right provides the analysis of the composition found.

Photograph apparently of material in centre hole of tray #1 of B column. Assays were primarily in the range 95-99% ZnO (zinc oxide), balance mainly zinc, with one sub-sample at 77.6% ZnO, 11.1% zinc silicate, 7.3% Zn and 4% zinc aluminate (overall analysis 95.9% Zn, 3.1% Si and 1% Al.)
These are similar to those for material found in the sump throat of 26 column (exploded 1996), figures for two samples being 97.8% and 97.2% ZnO.
[Ref: 15 & 16]

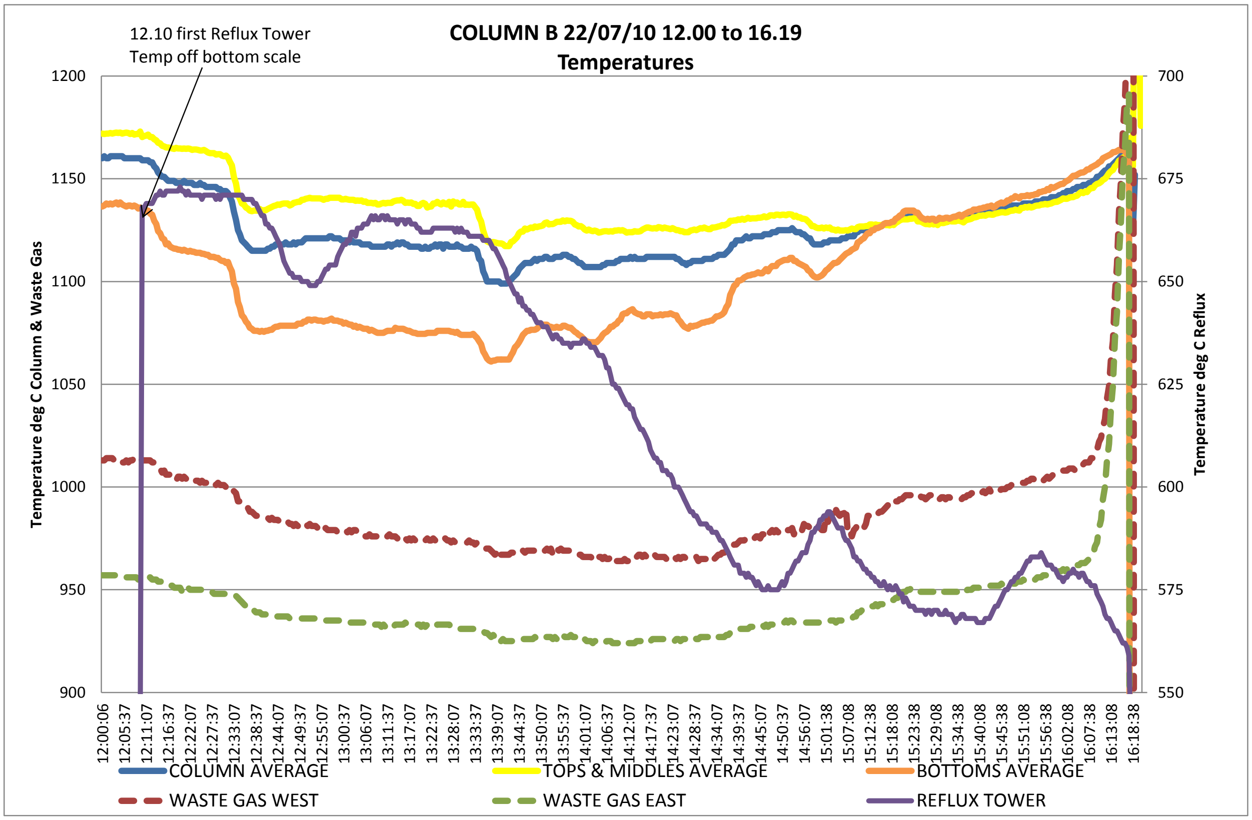
Reported for the January 1994 Noyelles-Godault explosion was also a similar plug [Ref: 1, p. 31], to quote *"A block of dross, porous with stalactites underneath could be seen plugging the first tray hole after the explosion in January, but it is thought that this kind of plug could have been produced after the explosion…"*

In my professional opinion the plug of oxide in tray #1 of column B was formed after the explosion, the mechanism being as follows. When the column exploded, trays collapsed onto #1 and vapour and liquid zinc down to tray #2 was largely thrown out into the workplace. Meanwhile the liquid zinc and dross, due to the partial blockage, still extended up the sump throat to tray#1. The plug partially formed whilst it was suspended by the blockage and then could grow further in situ. Subsequently the sump slowly drained, leaving a void in the throat.

Apparently material was found in the throat and in the sump at underflow level, but no report on this material has been made available.

IV.I.IV The Temperature Charts Created from [Ref: 10]; [Ref: 11]

Let us examine data for the last four hours of column B before the explosion. The chart below shows a summarised view of the column B temperatures over this period:



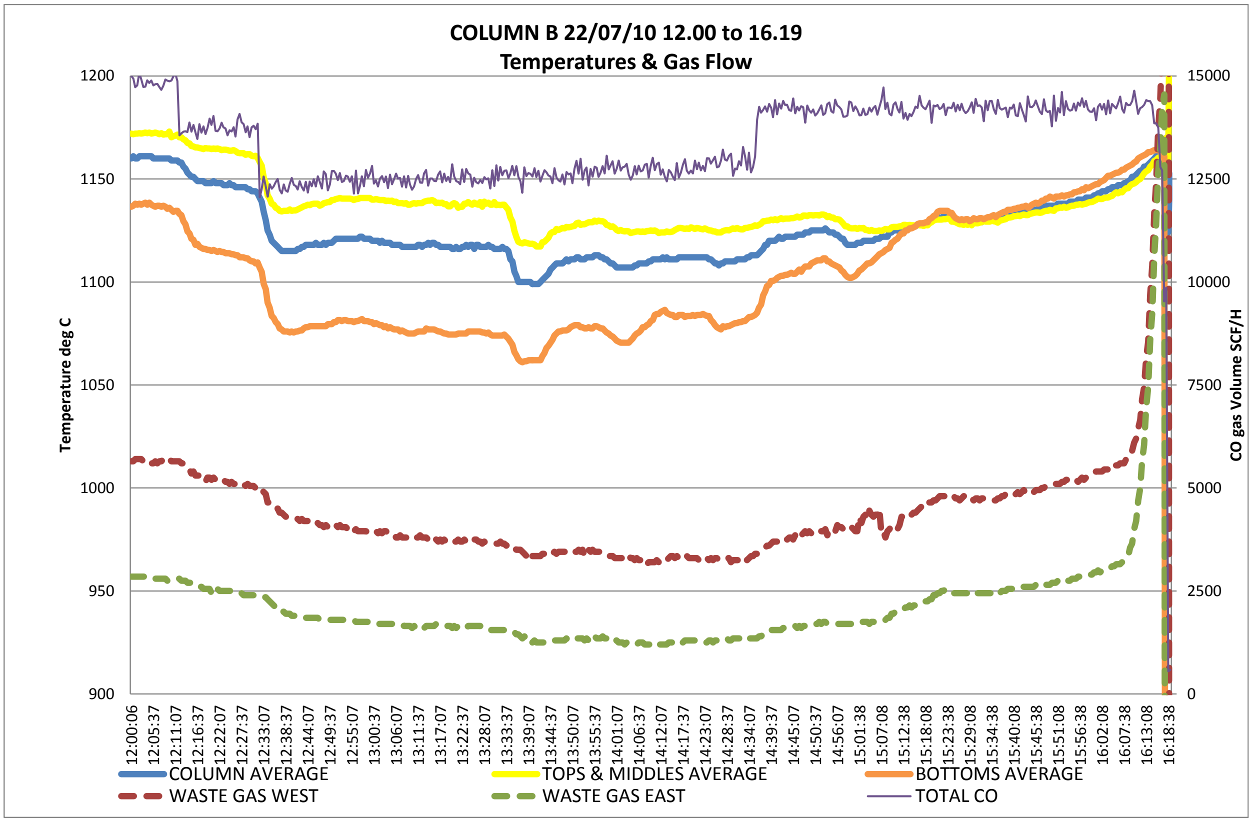
The points to note are:

- The first time that the reflux temperature (the control point for condensate) showed correctly in the life of the column was 12.10 on July 22 2010, just four hours before the explosion. In my professional opinion, for a key control thermocouple not to be available for a matter of days is not acceptable and is an example of inadequate attention to process control and safety. It contributed to the fact that condensate production had been far too high [Ref: Int. 11] up to this point, resulting in the operator reducing gas input (shown on the next chart).
- Temperatures are erratic, partly but not completely caused by changes to gas input.
- The reflux appears to have been lost, even with subsequent increases to gas input. This behaviour was noticed in the investigation [Ref: 1, p. 19] of the Noyelles-Godault explosion of January 1994. – to quote *"The crossover temperature stops oscillating and initiates a long decrease (from 700ºC to 500ºC in 2 hours)."*
- There is a worrying upwards trend in combustion chamber bottom and waste gas inlet temperatures from *at least* an hour before the explosion, with the bottom temperatures crossing from below the column and the tops and middles averages to above both averages. This behaviour was also reported by Monaca representatives [Ref: 9, p. C] in relation to the

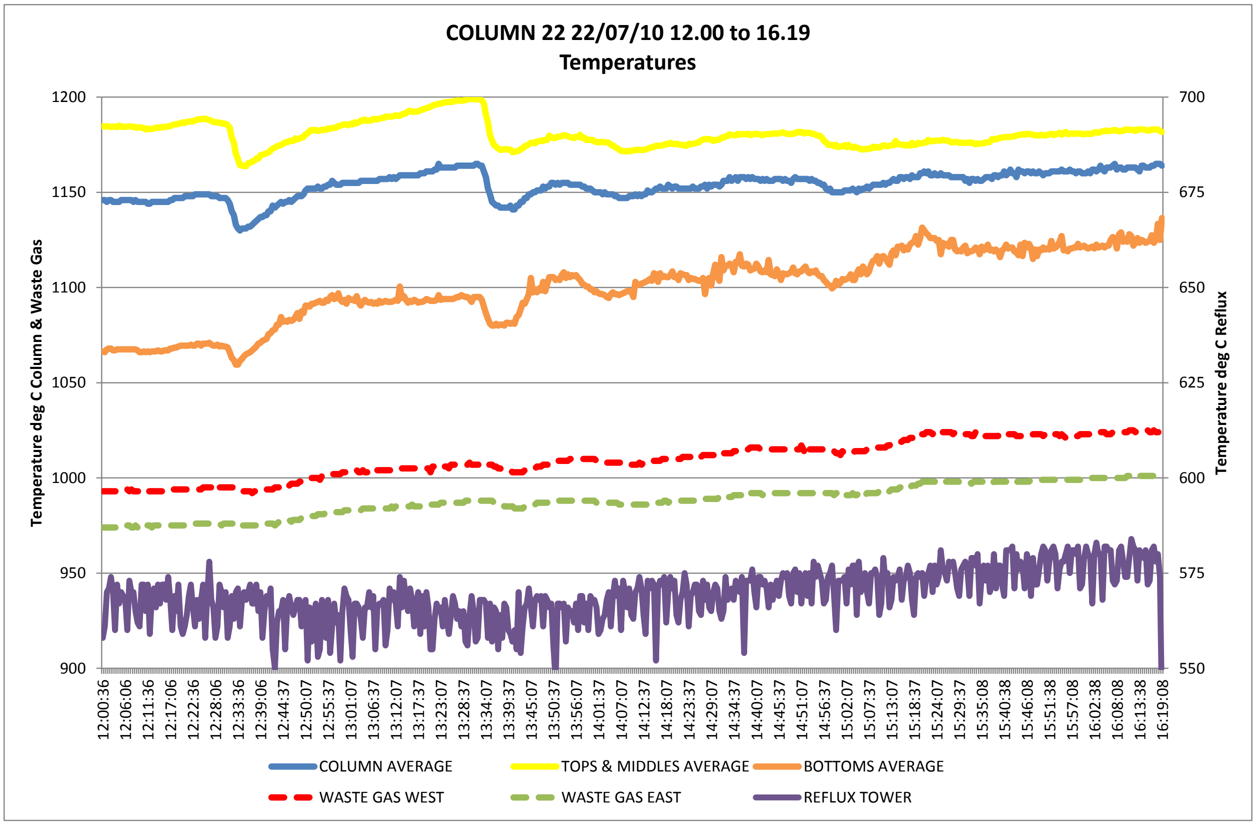
December 1993 explosion as *"waste gas and bottoms rising slowly,"* this being some three hours before *that* column exploded.

- The final part of the chart shows the "alarm" period leading to the explosion.

The second chart shows that the gas input changes will have influenced the temperature trends but, in my opinion, do not account for the rising *relative* trend of bottom and waste gas temperatures.



We can add a third chart for the same time period, but this time for number 22 column (also a cadmium column) so that we can compare "like-for-like" and note any similarities.

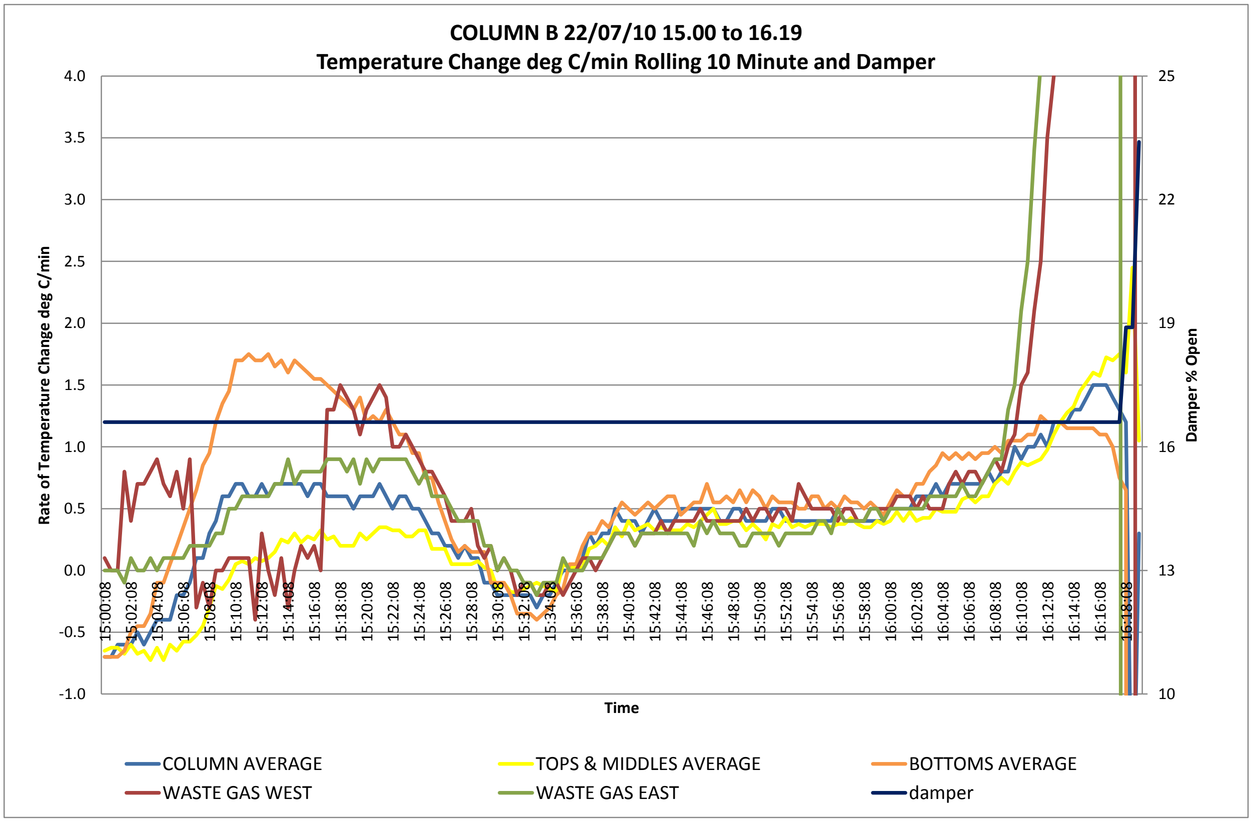


We learn the following from the above chart:

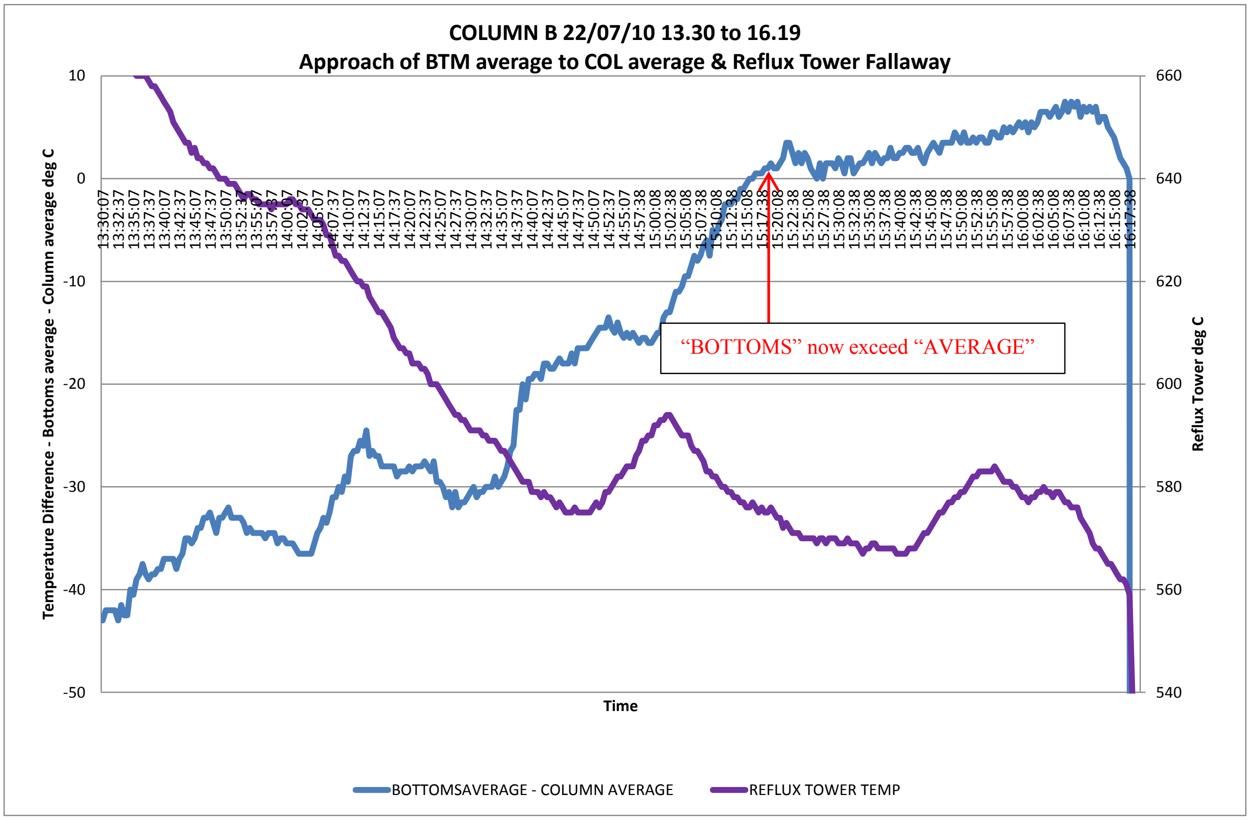
- One feature is common to both columns, this being the occasional dips and rises of temperatures *at exactly the same times*; this was almost certainly an external factor caused by changes in LCV (CO) gas calorific value. This was most undesirable, making column control (keeping quality of strip metal and amount of condensate in good balance) more difficult and rendering it less clear to see what was happening on the columns themselves. The impression from interviews [Ref: Int. 12] is that the controller "Flowcal" would bleed in natural gas automatically to maintain calorific value. Indeed, at a meeting of ZCA (a predecessor to Horsehead) with Indugas it was identified [Ref: 9 pH] that the heating value was maintained at 280 BTU/SCF by the calorimeter. On the other hand an operator [Ref: Int. 13] claims that the calorific value varied a lot and that it happened every day; the charts support the operator.
- The other feature of the chart is the low reflux temperature. Whilst column B was over-producing condensate, column 22 condenser had frozen. [Ref: Int. 14]
- It can also be seen that the trace for column 22 reflux was much more variable minute by minute than that for B.

We can look at the temperature changes on column B in more detail in the next chart which shows the rates of column and waste gas temperature change for the final 80 minutes. Note that the data in the chart are rolling 10 minute averages to smooth them – we are looking for rates of change often less than one degree/min but the raw data are only logged to the nearest whole degree.

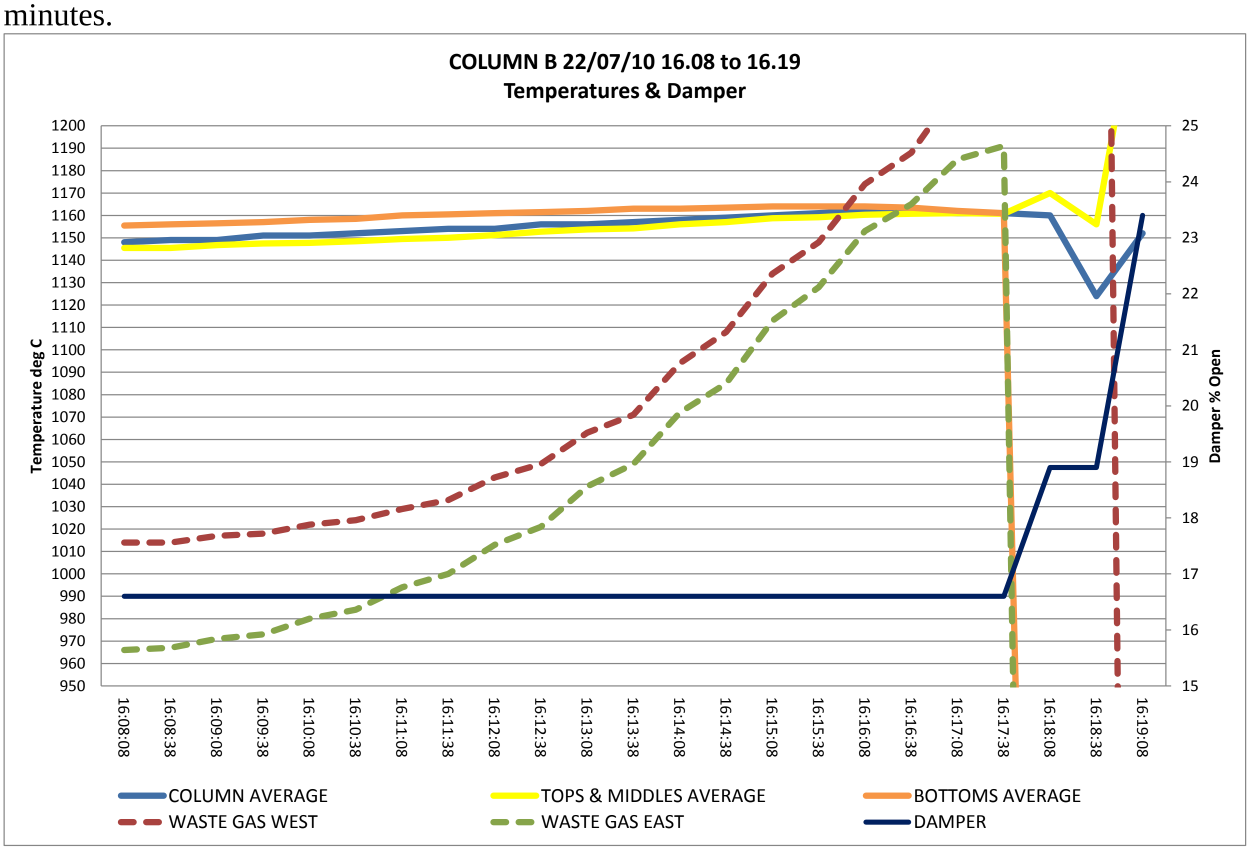
We can see that, leaving aside the final rapid rate of temperature rise (the alarm period), and a short period of relative stability around 15.30 to 15.36, all the column and waste gas temperatures were rising for a prolonged period at a significant rate. The bottom temperatures were rising at a slightly faster rate than the other temperatures.



Because *all* column temperatures were rising slowly it is easier to see the worrying trend by examining the *relative* movement of bottom temperatures compared with the column average in the chart below. The timescale of this rising of bottom temperatures (starting at around 13.30) is similar to the start of the decline in the reflux temperature.



The final chart shows B column temperatures and column damper position over the final 10 minutes.



Here we can see that the position of the bottom combustion chamber average temperature continues above the column average until the final moments of the column. It can be seen that in the final moments the damper starts to open, probably as a result of the failure of the suction gauge in the combustion chamber. It is therefore a matter of speculation as to whether the damper opening influenced the final explosion or not.

IV.II ANALYSIS OF THE DATA AND CAUSES OF THE EXPLOSION

In my professional opinion the following explanation shows clearly that column B partially blocked at the sump and backfilled with molten zinc and then exploded, this happening over the day to evening shift change period.

1. The most important factor in avoiding blockages is a sump design that allows liquid zinc and other inevitable materials like dross and pieces of brick and mortar to exit easily. Column B had a small underflow depth ("1 brick") that had proved to be too small in accidents around the world going back to 1973. The accidents at Noyelles-Godault France in 1993/1994 were on columns with "1 brick" underflows. As identified by a witness (Ref: Int. 15) *"Floating dross cannot get under the underflow……If a lot of dross is in the throat area, that gets just this side of impossible to get it out."*

   My information from a 2007 Refinery Safety Survey [See Appendix III question C13 (Ref: 19)] carried out on behalf of Horsehead, indicated that the underflow clearance was at least "2 bricks." *(It is not appropriate for me to divulge individual figures for participants but Horsehead was not the 85mm figure and was therefore in the range 145-200mm).* It is therefore unexplained how the 2010 B column sump had the dimension $2^5/_8$in (65mm). A possible explanation is that the dimension in the 2010 drawing may have found its way in from an old out-of-date drawing.

   The design of the feed, with the flow through the needle valve "top down" rather than "bottom up," would not minimise dross and air entrainment in the liquid zinc entering the column.
2. B column was operating as a cadmium column, its last run having been as a zinc oxide column. Oxide columns operate under a very different scenario – run-off rates only a quarter to a fifth of those for cadmium columns and a much higher iron level. Quoting Monaca representatives in 1994 [Ref: 9, p. 15] *"Cadmium columns"* (believed to be misprinted in the document and should be *"Zinc oxide columns"*) *"have a feed of 55 t/d containing 0.03-0.04% Fe and the concentration is fourfold."* This implies a run-off containing 0.14% Fe, at which level the quote continues *"Blockage of the sump with iron containing materials is a problem."* B column had been prematurely shut down due to sump blockages (Ref: Int. 16) and, since the sump was not sufficiently clear to allow the sump burner to function correctly on heat-up, the evidence suggests that residual material remained in the sump on start-up. Given that liquation pots were not always operated at a low enough temperature to remove iron to harmless levels, it is evident that iron levels in run-off from oxide columns could be high enough to deposit hard zinc in the sump passages. The concentration ratio (feed to run-off) in the oxide columns was, on conservative assumptions, about 2.3. This consistent situation at Horsehead Monaca probably explains the regular problems with sumps and the history of explosions and "near-misses" on oxide columns.
3. The warm-up for column B was unsatisfactory. The sump burner was not operating properly,

yet this is so important. The only way that any new sump brickwork or the mortar for the bottom tray can be dried properly is from hot sump burner gases passing *inside* the column and up to the top by natural draft. Any moisture left when metal was fed would react and create thick pasty dross. It can be noted here that the location of Monaca means that air humidity is generally high in July, and 2010 was no exception. For the two weeks from column feed to the explosion, average daily dew point was 21ºC [*Source – Wunderground.com – for KBVI - Beaver County Airport, PA*], meaning that air drawn into the column would contain some 18 gm moisture/m^3 or more. This is another potential contributor to pasty dross.

4. It appears that problems still persisted with the sump after commissioning. The sump was found leaking on several occasions (a symptom of partial blockage – the test being to cut feed rate and observe if the leak slows or stops) and had to be strapped. Given this history, Horsehead Monaca management should have put out a general warning that B column was functioning abnormally, that there was a potentially hazardous condition at the sump and that extra care should be taken. To quote from the international investigation into the 1993 and 1994 French accidents [Ref: 1 page 52], when reviewing a number of previous incidents, *"Note that several of known accidents with explosions were preceded by difficulties at the sump. This was also the case for the two accidents at Noyelles-Godault."* The ladle log shows a steadily increasing feed to B column which is perfectly normal for the commissioning of a new column but, if the sump was partly restricted, it represents an increasing possibility that it might not cope with the flow of liquid zinc. At its peak shortly before the explosion it would appear that the column was operating at approximately 110 st/d, a high rate compared to standards within the industry. In most operations cadmium loads are much heavier, and cadmium removal requires more intensive boiling, so that feed rate would not be more than 60-65 t/d.
5. The temperature charts constructed from the DCS data show a clear anomaly with the B column temperatures from at least an hour before the explosion; bottom and waste gas temperatures were rising, the former to a point higher than the column average. This cannot be explained by variations in CO gas quality or the changes to gas input to B column. It is not clear as to why this was not observed on the control room computer screen – it is understood that the paper chart recorders for the main column temperatures no longer worked [Ref: Int. 17], but that the charts were on the bottom of the computer screen [Ref: Int. 18]. The number of individual combustion chamber thermocouples combined with their temperature movements due to gas quality changes would, however, have made it more difficult to see the clarity obtained from the penultimate chart in section IV.I.IV. This still raises the question as to what training operators had been given to recognise these temperature trends as indicating possible blockage and backfilling.
6. Using volumetric data for the sump throat, tray #1 and trays #2-7 provided by CEC [Ref: 17, p. 23] a calculation can be made for the time taken for the column to backfill to tray #7 – a useful reference point for creating a raised pressure at the bottom of 1 atmosphere and associated raised zinc boiling point (907ºC to 980ºC). If we assume a feed rate of 110 t/d with still a very healthy (by appearance) run-off (strip metal) flow of 50 t/d (twice that from oxide columns), and that an irregularity in combustion chamber temperatures will not show until the backfill reaches tray #1, the time taken to reach tray #7 would be less than one and a quarter hours. This figure is of the correct order of magnitude to satisfy the temperature chart deviations, to allow a substantial and dangerous backfill of the column and to still allow the run-off to appear reasonably normal.
7. There is also a clear anomaly with the reflux temperature which was moving in the opposite

direction to the column temperatures. The slowly rising bottom and waste gas temperatures and the falling reflux temperature are entirely consistent with what would be expected if the sump was partly blocked and the column backfilled with liquid zinc; the bottom and waste gas temperatures would rise due to the higher temperatures inside the column and the reflux would become "detached" due to reduced vapour production as a result of the high pressure within the liquid zinc. This is the classic **"Pressure Cooker"** – *the column becomes an energy store at an elevated temperature with a limited ability to release energy in the form of vapour*.

8. The high rate–of-change alarm warned that the column was in imminent danger 10 minutes before it exploded, but there appears to have been no specific alarm to draw attention of the operator to the subtle but dangerous temperature changes that were taking place much (i.e. hours) earlier. Although there were key temperature charts available on the computer monitors, in my opinion, the traditional paper charts can be better at drawing attention to the differences between the columns and the worrying signs of problems building up. Having said that, it should be possible to design a more modern control system that could draw attention to trends that are potentially hazardous.
9. The only action that might have saved the day would have been a drastic cut in feed rate, to allow the backed-up liquid zinc an opportunity to clear the sump. After the final alarm it almost certainly would have been too late, but there was a period of hours of column backfilling prior to this when it should have been effective.
10. When the column exploded there can be little doubt that it happened under the ***"Pressure Cooker Explosion"*** scenario. In the case of a cadmium column, events would occur faster than on an oxide column, because run-off (strip metal) flow was four to five times higher. Thus the sump partially blocks, liquid metal builds up in the column, pressure and hence the boiling point of the zinc rises and finally something has to give. The high rate of temperature change alarm signalled the leakage of zinc and its combustion – *"the ring of fire"* described by an operator [Ref: Int. 8]. The explosion that destroyed the blow-out panels almost certainly destroyed the combustion chamber pressure probe, because the opening of the column waste gas damper appears to be in response to a zero reading rather than to a real pressure change.
11. In the aftermath of the explosion, the reflux section appears to have been "disconnected" from the boiling section – the relief bricks at the column top did not blow [Ref: Int. 19] and the reflux section, albeit now sitting on the combustion chamber roof, was largely undamaged.
12. The analysis of material found in the bottom tray was primarily zinc oxide, with small traces of silicate and aluminate, which would have come from mortar or tray debris. It is most likely that this was formed *after* the explosion. The main sump blockage was, in my opinion, likely caused by a zinc oxide plug restricting the flow much lower down under the sump underflow.

IV.III WHAT ALTERNATIVE SCENARIOS COULD HAVE CAUSED THE EXPLOSION

1. In my professional opinion, all the symptoms of this accident are consistent with expected features of the ***"Pressure Cooker Explosion"*** and not the following alternatives.
2. An explosion as a result of a normal leak has been proposed [Ref: 13]. But a column operating normally will not blow up, even if it is suffering wear and tear and leaking zinc [Ref: Int. 19] – to quote *"If a column leaks molten zinc or vapour it would not cause an explosion. I have repaired both over many years and never had an explosion."* The combustion of zinc from

normal leaks would not have sufficient pressure to blow out the combustion chamber walls and the volumes of zinc that were involved could only occur from a column that had backfilled with liquid zinc. A further proposal [Ref: 14] is made on similar grounds.

3. The proposal [Ref: 13] also suggested that the mortar jointing the column trays was not of the appropriate quality, part of the evidence being solidified liquid zinc in tray joints. However, under normal operation the liquid zinc would not reach joint level (i.e. it would only be there if the tray was full of liquid zinc) and the joint would never be expected to have the same strength as the trays themselves.
4. A gas explosion is another possibility. However the operating temperature of the combustion chamber is outside (above) the explosion limit for the gas.
5. A collapse of trays can be ruled out as a *first* cause of the explosion. The mechanical strength of tray material is high. Certainly the boiling trays collapsed, but this was as a *result* of the explosion, not as the cause. The slow temperature movements in the hour or more prior to the explosion, coupled with no evidence of leakage throughout this period, are not consistent with a collapse.
6. It has been suggested [Ref: 17, p. 25] that the blockage was caused by mortar “peels” obstructing the centre hole of the tray #1 resulting from inadequate removal during column construction. However, whilst “peels” are undesirable, no direct evidence of peels or significant amounts of materials arising from them were found on column B, and those columns that were found with “peels” did not explode. Hence there was no link between “peels” and column B. In any case mortar has a specific gravity between a third and a half that of zinc and peels would therefore float buoyantly *on the surface* of any zinc and not underneath it. It was also claimed that the design of tray #1 was defective [Ref: 17, p. 28] in that it was too cold; but this claim, in my opinion, misunderstood the purpose of tray #1, and the temperature claim was not correct. This same report suggests [Ref: 17, p. 23] that, since the operator noted no sump blockage 30 minutes before the explosion, the blockage occurred immediately afterwards in the hole in tray #1, with the run-off stopping altogether, and then zinc backfilled up to the middle of tray #3, whereupon the column exploded. In my opinion these conclusions are flawed as they are not supported by the evidence.

V. PROCESS MANAGEMENT

The foregoing sections provide a complete analysis of the technical factors behind the explosion. However, in my professional opinion, human factors played a crucial role. The zinc refining process is made more difficult by the fact that instrumentation is limited. Learning from experience, including that of others, is important. Indeed, that was the purpose of the 1994 Bristol UK conference held after the international investigation of the Noyelles-Godault France accidents that occurred in July 1993 and January 1994.

In my professional opinion, in order to reach the point of explosion of column B in 2010, Horsehead Monaca process management had to pass through five sets of traffic lights that could be entitled “PAUSE FOR THOUGHT.” These are shown below:

PAUSE	THOUGHT	REMEDIAL ACTION
1. Premature shutdown of “B” in June 2010 and explosion “near-miss”	Have we lost our technical competence? This is not our first serious blockage	Review EVERYTHING from ground up – sump design to operating procedures
2. Premature shutdown of “B” in June 2010 – Blocked sump	Must not restart “B” unless certain that sump is clear	Check and if necessary rebuild sump before column rebuild
3. Sump Burner not heating column on start-up - Blockage	Sump not clear. Column MUST be commissioned properly	Delay heat-up until issue rectified and danger removed
4. Sump leaks and blockages after feed started	Column is online but functioning abnormally	General warning for EXTREME CAUTION
5. Two hours of rising “Bottoms” and falling “Reflux Tower”	Column is backing up with liquid zinc	Cut feed – Emergency plan - Prepare for shutdown if sump not cleared

Missing these critical points indicates that, in large measure, hazardous conditions at Monaca had been “normalised” and that process management had become desensitised to what was going on. This raises the question as to whether sufficient technical support was provided to the plant on a regular basis.

VI. Conclusions

My professional opinion is that the evidence, facts and my analysis lead to the following conclusions:

1. The explosion and fire on column B at Horsehead Monaca in July 2010 was an example of a ***"Pressure Cooker Explosion."*** A partly restricted sump allowed liquid zinc to build up in the column which eventually exploded.
2. The Monaca B column sump design with a small clearance under the underflow ("1 brick") had been historically a significant factor in serious incidents around the world.
3. Column B had a poor start-up. The previous column (as an oxide column) was shut down owing to sump blockages and it appears that the sump was not properly cleared at the rebuild, *the evidence being that the column sump would not allow passage of the gases from the heat-up burner; hence sump recorded temperatures were never satisfactory*.
4. During the days of operation prior to the explosion there were a number of instances of sump leaks and other indications of blockages, and the sump had to be "strapped" on several occasions.
5. The above factors pre-disposed this column to blockages at the sump. The column was not operating normally but there was no general warning to employees to that effect. Yet the feed rate was steadily being increased, placing a progressively higher volume load on the sump.
6. In the period of at least an hour, probably two hours, prior to the explosion, combustion chamber bottom and waste gas temperatures took slow upwards trend that are associated with backfilling and the raising of the zinc boiling point under pressure. In addition the reflux temperature took a trend downwards which is also what might have been expected under this scenario. The duration of the temperature changes fits well with what would be required for a significant backfilling of the column.
7. The absence of *paper* chart recorders for the main temperatures of each column meant that the subtle changes taking place may not have been observed on the computer screens by operators. The fact that CO gas BTU quality was varying would have added to the difficulty in interpreting what was going on. Whilst the refining process is difficult to fully instrument, a more modern SIS "safety instrumented system" should allow predictive algorithms to warn of conditions that are hazardous. But, if operators were not trained to recognise these symptoms of blocking and backfilling, it is unlikely that the computer could have been programmed to do this either.
8. When the rate-of-change alarm first sounded 10 minutes before the explosion this was signalling imminent danger. The high rate of temperature change alarm was signalling that zinc, under internal pressure in the column, was leaking and burning.
9. Under extreme pressure the tray wall(s) eventually failed, releasing a large volume of zinc vapour and superheated zinc that would flash to vapour, and this pressure pushed out the combustion chamber blast panels. The zinc spray and vapour now had access to large amounts of workplace air and this created a massive zinc flame across the workplace.
10. The fact that the liquid zinc back-up and the explosion occurred unusually on a cadmium column is probably a reflection of its poor start-up combined with a high run-off (strip metal) rate (~110 st/d) compared to an oxide column (~25 st/d). The prevalence of sump problems and explosions on oxide columns at Monaca is probably a reflection of a high concentration of iron in run-off, aggravated by questionable (i.e. log sheets suggest inadequate control) liquation pot temperature control. To quote from the international investigation into the 1993 and 1994

French accidents [Ref: 1 page 30], when reviewing a number of previous incidents, *"Sump problems are experienced generally on columns treating a zinc with high content of impurities like iron, which can precipitate solid compounds even at high temperature. This is the case for the lead columns and for the reboilers where impurities are concentrated. Very few blockages are reported on the cadmium columns."*

11. The scenario described above is the only one that is fully consistent with the witness statements, with control system data from the plant, from information from past incidents and from an understanding of zinc and its properties and behaviour.
12. The accident happened in large measure because hazardous conditions (Sump Blockage and its symptoms) had become "normalised" by process management.

A very simple explanation of what happened and why can be obtained by examining the properties of zinc, as follows:

- *Liquid zinc* oxidises and creates dross in the presence of air, the rate increasing at higher temperature, but it does not burn as such or explode. There are many thousands of furnaces holding liquid zinc around the world and none of them spontaneously ignites or explodes.
- *Leaked liquid zinc* can sit at the bottom of the combustion chamber and will burn away very slowly. I suspect that the burning follows evaporation which can happen because the ambient temperature is some 1150^{0}C – what I mean by this is that, to burn as a flame, the zinc needs to be in vapour form; this evaporation is quite slow due to the fact that the latent heat of evaporation has to be provided first from the hot combustion chamber.
- *Zinc vapour* will burn spontaneously in a self-sustaining way with a very intense flame – hence the oxide column blow-box where zinc burns rapidly.
- The above factors mean that the only way to obtain a zinc "explosion" is from a *sudden release of a large amount of vapour*. Thus we have to have a store of energy in the form of vapour or incipient vapour (superheated zinc) to cause such *a rapid decompression* and fire that occurred. This in turn can only arise from the column backfilling and being "charged up" with energy. Calculations show that the normal production rate of vapour in a cadmium column is of the order of 20-25 t/d, or around 16 kg/*minute, or 0.25 kg/second*. This *rate* provides a large flame (slightly less than a normal blow-box). However a column flooded with several tonnes of liquid zinc to tray 7 (1.5 m) would release an additional **50 kg** *almost instantly*, this figure increasing to **125 kg** for a 15 tray (3 m) flooding. These figures, resulting from rapid decompression, are several orders of magnitude higher.
- The heat released from the combustion of this zinc vapour is more than enough to create more vapour from the remaining liquid zinc and to sustain a powerful flame for a considerable period of time (the Horsehead security video shows some five to ten minutes of *very* intense smoke emission from the building).

VII. PREVENTION OF "PRESSURE COOKER EXPLOSIONS"

VII.I DISADVANTAGES OF THE PROCESS

- Mortar joints for the trays will never be completely perfect – some vapour leakage is inevitable.
- Silicon carbide has a low resistance to thermal shock. Very steady operating conditions are needed and, even with this, some tray cracks are inevitable – and more leakage, increasing as the column ages.
- It is difficult to instrument this process. Finding probes that will work at high temperature is difficult; leakage forms zinc oxide, which can block probes or cover them with a film of oxide. Any window for observation will similarly cloud over. Leakage of liquid zinc will attack anything containing iron.
- Much of the difficulty in operation relates to knowing what is going on inside. It requires a lot of experience and some technical knowledge to be competent.
- A history of sump blockages, partial or total, resulting in backfilling of columns and hence unexpected operation outside the design conditions is a sign that the operation is not under control. Ultimately, on some occasion conditions will combine such as to cause a breach of the column wall and an explosive release of zinc liquid, spray and high-pressure vapour.

VII.II PHYSICAL IMPROVEMENTS

- Following the French accident investigation, some recommendations were made, principally to ensure that the column sump underflow clearance is at least "2 bricks" which is around 130 mm rather than 65 mm, to install vibration meters on the column and to install load cells under the column to enable an immediate determination of backfilling.
- Some of these changes were implemented at Horsehead Monaca and all at Noyelles-Godault France, prior to restarting operations. Noyelles-Godault suffered no further similar failures up to the plant closure in 2003 (for economic reasons).
- A colleague on the international investigation team was involved as a key designer for the new plant built at Huta Cynku – Miasteczko Slaskie in Poland in 1999. This incorporated what one might call the best-known technology and could be regarded as "state of the art". In particular this plant incorporated load cells under each column, temperature measurement of run-off, dust load in waste gases, vibration monitors in three directions on sumps and oxygen analysis on waste gases. These data are shown on a mimic screen. This was the situation when I visited in January 2007. All of these changes provide operators with better knowledge of what is happening. This plant is currently being expanded, expected completion due in June 2015.
- If the symptoms of impending problems can be documented, such as the slow rise of bottom combustion chamber temperatures towards the average, and can be incorporated in algorithms, then a modern SIS "safety instrumented system" can be programmed to warn of trouble.
- Physical barriers to prevent access to areas that would be hazardous in the case of an explosion, or vented explosion panels, have their place, but if access is restricted too severely, then normal legitimate activity (for example the replacement of column thermocouples and "Column Work") can be inhibited. Certainly the platforms providing

access to the combustion chamber wall should have locked entrances, and a "permit to work" system, whereby the supervisor first carries out a risk analysis before allowing entrance, and anyone entering must be in contact with the control room at all times.

VII.III Process Management Improvements

- There is no currently available new technology to replace the New Jersey Process for refining metallic zinc. But there are many plants that have not had the type of accident experienced by Horsehead Monaca. In my opinion, by incorporating the latest improvements and by ensuring that all operators are exceptionally well trained, the process can be operated safely.
- Training is critical. Operators are more than capable of understanding the process and its hazards and the symptoms that signal enhanced risk. It is disturbing that the ground- and first-floor operators such as those tending the sumps can be the least-well trained, yet the sump itself is a hazardous place. These operators may not be fully aware of what operators controlling the columns on the feed floor *are* aware of or what actions they are taking that could affect the sumps. Operators are present "24/7" and, to stay safe, must have sufficient technical knowledge to recognise symptoms and act with the understanding that a professional process engineer would have.
- Steady operation, particularly of feed rate and firing, not only provides steady conditions and a long column life with less leakage, but it also helps to avoid the fluctuating conditions that can allow air to enter the column and lead to further difficulties. My preference is to control the firing of columns on a target of fuel input rather than temperature – in this way *any* temperature excursion is giving a signal that something has changed. It follows that fuel, even if it is the by-product of smelting and is so-called "free," must have a constant calorific value. It should be possible to achieve this by modern calorimetric control, and possibly the ETF plant at Monaca could have scheduled maintenance in a less disruptive way. If not, then possibly the on-site thermal power station would have been a more appropriate customer for the furnace gas.

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7 CSB – 27 July 2010; 2 November 2010; OSHA - 4 August 2010.
8 OSHA – 6 August 2010.
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12 OSHA – 29 July 2010; CSB - 17 August 2010.
13 CSB – 28 July 2010.
14 CSB – 28 July 2010.
15 CSB – 3 November 2010.
16 CSB – 2 November 2010; 28 July 2010.
17 CSB – 28 July 2010.
18 CSB – 28 July 2010.
19 OSHA – 28 July 2010.

NOTES

1 The word "Explosion" has been loosely used to express what most people would call a "big bang"; technically, however, an explosion normally infers an instantaneous detonation of a mixture of a flammable material and air or oxygen *that has to occur within a specific range of composition and temperature.* The Horsehead event was not an explosion in that sense and could better be described as an *"explosive decompression and conflagration."*

2 *Pressures* (e.g. one bar or atmosphere) are, in this report, expressed *relative to atmospheric pressure*. Thus one atmosphere means "one atmosphere *above* atmospheric pressure," which pure scientists would call two atmospheres."

IX. APPENDICES

APPENDIX I COLUMN HEAT-UP LOG

CSB – 1Doc-03 – 0
.5 col

To: Tom Simon / Operations
Supervisors / Operations
Feed Operators / Operations
B. Belli / Electrical
F. Grabski / Maintenance
Eric Clark / Maintenance
Keith Richter / Bricklayers
J. Dechellis / Furnace Plant

From: M. Orehowsky

Subject: Column Heat-Up and Start-Up Dates

No. B Column

Heat-up will begin: 06/30/10

Start-up will be: 07/10/10

CONFIDENTIAL HorseheadCSB0000507

No. B COLUMN 10-DAY HEAT-UP SCHEDULE

Rate 4 DEGREES PER HOUR

DATE: 30-Jun 2010 **DAY 1**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00				
8 :00				
9 :00				
10 :00				
11 :00	**Light 4" Maxon burners in the two**			
12 :00	**outside bottom cleanout holes.**			
1 :00	**Open nostril box covers about 3/8".**			
2 :00	**Light the 4" burner in the waste gas also.**			
3 :00	**Do not light the sump burner.**			
4 :00		60		
5 :00		60	–	–
6 :00		64	–	–
7 :00		68	–	–
8 :00		72	–	–
9 :00		76	–	–
10 :00		80	–	–
11 :00		84	–	–
12 :00	—	87	–	–
1 :00		91	–	–
2 :00	—	95	–	–
3 :00		99	–	–
4 :00	—	103	–	–
5 :00		107	–	–
6 :00	—	111	–	–

DATE: 01-Jul **DAY 2**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		115	–	–
8 :00	—	119	–	–
9 :00		123	–	–
10 :00	—	126	–	–
11 :00		130	**Light a 2" Maxon**	
12 :00	—	134	**burner at the sump.**	
1 :00		138	**Do NOT use larger**	
2 :00	—	142	**(3" or 4") burners,**	
3 :00		146	**until DAY 6.**	
4 :00	—	150		64
5 :00	**Light a 2"**	154		68
6 :00	**burner in the**	158		71
7 :00	**crossover.**	161		75
8 :00	—	165		78
9 :00		169		82
10 :00	—	173		85
11 :00		177		89
12 :00	—	✓ 181		92
1 :00		185		96
2 :00	—	✓ 189		99
3 :00		193		103
4 :00	—	✓ 197		106
5 :00		200		110
6 :00	—	204		113

Flame safety devices must be used on ALL burners during column heat-ups.

Reference: Starting-up New Columns, I-PC-09-0108

Date Issued: 06/30/10 Page 1 of 6 **Approved by:**

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DATE: 02-Jul **DAY 3**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		208		117
8 :00	—	212	—	120
9 :00		216		124
10 :00	—	220	—	127
11 :00		224		131
12 :00	—	228	—	134
1 :00		232		138
2 :00	—	235	82	141
3 :00		239		145
4 :00	—	243	42	148
5 :00		247		152
6 :00	—	251	44	155
7 :00		255		159
8 :00	320	259	49	162
9 :00		263		166
10 :00	—	267	109	169
11 :00		271		173
12 :00	—	274	52	176
1 :00		278		180
2 :00	—	282	51	183
3 :00		286		187
4 :00	—	290	—	190
5 :00		294		194
6 :00	—	298	—	197

DATE: 03-Jul **DAY 4**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		302		201
8 :00	—	306	46	204
9 :00		309		208
10 :00	—	313	46	211
11 :00		317		215
12 :00	—	321	45	218
1 :00		325		222
2 :00	—	329	46	225
3 :00		333		229
4 :00	349	337	72	232
5 :00		341		236
6 :00	353	344	75	239
7 :00		348		243
8 :00	361	352	56	246
9 :00		356		250
10 :00		360	77	253
11 :00		364		257
12 :00	—	368	74	260
1 :00		372		264
2 :00	—	376	68	267
3 :00		380		271
4 :00	—	383	68	274
5 :00		387		278
6 :00	—	391	68.	281

Flame safety devices must be used on ALL burners during column heat-ups.

Reference: Starting-up New Columns, I-PC-09-0108

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 HorseheadCSB0000509

DATE: 04-Jul **DAY 5**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		395		285
8 :00	—	399	69	288
9 :00		403		292
10 :00	**Light**	— 407	92	295
11 :00	**Reflux**	411		299
12 :00	see note below	— 415	59	302
1 :00		418		306
2 :00	—	422	56	309
3 :00		426		313
4 :00	381	430	56	316
5 :00		434		320
6 :00	433	438	56	323
7 :00		442		327
8 :00	514	446	55	330
9 :00		450		334
10 :00	548	454	270	337
11 :00		457		341
12 :00	524	461	283	344
1 :00		465		348
2 :00	542	469	295	351
3 :00		473		355
4 :00	550	477	297	358
5 :00		481		362
6 :00	555	485	301	365

Day 5: Light a 2" burner at the feed tube to heat the reflux tower. Make sure the flame is pulled into the feed tube. The crossover must be open to get draft to pull the flame into the feed tube.

DATE: 05-Jul **DAY 6**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		489		369
8 :00	570	492	297	372
9 :00		496		376
10 :00	582	500	295	379
11 :00		504		383
12 :00	593	508	299	386
1 :00		512		390
2 :00	601	516	301	393
3 :00		520		397
4 :00	612	524	301	400
5 :00		528		404
6 :00	620	531	304	407
7 :00		535		411
8 :00	628	539	309	414
9 :00		543		418
10 :00	636	547	311	421
11 :00		551		425
12 :00	638	555	**Switch to**	313 428
1 :00		559	**a 3" burner**	432
2 :00	645	563	**on sump.**	318 435
3 :00		566		439
4 :00	650	570	320	442
5 :00		574		446
6 :00	652	578	320	449

Flame safety devices must be used on ALL burners during column heat-ups.

Reference: Starting-up New Columns, I-PC-09-0108 **Page 3 of 6**

B

 HorseheadCSB0000510

B

DATE: 06-Jul **DAY 7**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		582		453
8 :00	663	586	322	457
9 :00	**Light**	590	**Light**	460
10 :00	**Feedpot**	672 594	**Liquation**	324 464
11 :00		598	**Pot**	467
12 :00	681	602	334	471
1 :00		605		474
2 :00	672	609	337	478
3 :00		613		481
4 :00	700	617	339	485
5 :00		621		488
6 :00	709	625	344	492
7 :00		629		495
8 :00	714	633	312	499
9 :00		637		502
10 :00	721	640	213	506
11 :00		644		509
12 :00	724	648	309	513
1 :00		652		516
2 :00	733	656	380	520
3 :00		660		523
4 :00	747	664	288	527
5 :00		668		530
6 :00	754	672	—	534

DAY 7:

Light feedpot burners.

Light liquation pot burners.

DATE: 07-Jul **DAY 8**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		675		537
8 :00	759	679	63	541
9 :00		683		544
10 :00	761	687	26	548
11 :00		691		551
12 :00	767	695	44	555
1 :00		699		558
2 :00	771	703	—	562
3 :00		707		565
4 :00	776	711	—	569
5 :00		714		572
6 :00	778	718	—	576
7 :00		722		579
8 :00	781	726	—	583
9 :00		730		586
10 :00	788	734	—	590
11 :00		738		593
12 :00	789	742	135	597
1 :00		746		600
2 :00	784	749	219	604
3 :00		753		607
4 :00	783	757	229	611
5 :00		761		614
6 :00	783	765	233	618

Day 8:

Light a 3" burner n the cleanout hole of the condenser.

Flame safety devices must be used on ALL burners during column heat-ups.

Reference: Starting-up New Columns, I-PC-09-0108 Page 4 of 6

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D

DATE: 08-Jul **DAY 9**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		769		622
8 :00	785	773	230	625
9 :00		777		629
10 :00	789	781	225	632
11 :00		785		636
12 :00	791	788	220	639
1 :00		792		643
2 :00	796	796	213	646
3 :00		800		650
4 :00	799	804	209	650
5 :00		808		650
6 :00	803	812	202	650
7 :00		816		650
8 :00	818	820	195	650
9 :00		823		650
10 :00	844	827	192	650
11 :00		831		650
12 :00	849	835	186	650
1 :00		839		650
2 :00	855	843	180	650
3 :00		847		650
4 :00	860	851	—	650
5 :00		855		650
6 :00	848	859	—	650

DATE: 09-Jul **DAY 10**

TIME	Column Actual	Column Target	Sump Actual	Sump Target
7 :00		862		650
8 :00	854	866	—	650
9 :00		870		650
10 :00	861	874	54	650
11 :00		878		650
12 :00	866	882	55	650
1 :00		886		650
2 :00	868	890	55	650
3 :00		894		650
4 :00	867	897	54	650
5 :00		900		650
6 :00	866	900	47	650
7 :00		900		650
8 :00	870	890	74	650
9 :00		880		650
10 :00	876	870	49	650
11 :00	**TOP**	860		650
12 :00	**FIRE** 884	850	37	650
1 :00	see note below	840		650
2 :00	844	830	36	650
3 :00		820		650
4 :00	774	810	20	650
5 :00		800		650
6 :00	768	790	10	650

Day 9: Melt Cd slabs to fill the condenser bowl and seal the underflow

Day 10: Feedpot should be at 600 - 650C for priming column.

Note that the column temperature starts to cut back 10 deg. per hour at 7pm.

For TOP FIRE see steps 6 through 11 in Starting-up New Columns , I-PC-09-0108.

Reference: Starting-up New Columns, I-PC-09-0108 Page 5 of 6

CONFIDENTIAL HorseheadCSB0000512

DATE:	10-Jul	DAY 11			DATE:	11-Jul	DAY 12
TIME	Column Actual	Column Target	Sump Actual	Sump Target	TIME	Column Actual	Column Target
7 :00		780		654	7 :00		1160
8 :00	790	770		657	8 :00		1170
9 :00	START	760	/	661	9 :00		1170
10 :00	FEED	782 750		664	10 :00		1170
11 :00		750		668	11 :00		1170
12 :00	794	770		671	12 :00		1170
1 :00		790		675	1 :00		1170
2 :00	810	810		678	2 :00		1170
3 :00		830		650	3 :00		1170
4 :00		850		650	4 :00		1170
5 :00		870		650	5 :00		1170
6 :00		890		650	6 :00		1170
7 :00		910		650	7 :00		1170
8 :00		930		650	8 :00		1170
9 :00		950		650	9 :00		1170
10 :00		970		650	10 :00		1170
11 :00		990		650	11 :00		1170
12 :00		1010		650	12 :00		1170
1 :00		1030		650	1 :00		1170
2 :00		1050		650	2 :00		1170
3 :00		1070		650	3 :00		1170
4 :00		1090		650	4 :00		1170
5 :00		1110		650	5 :00		1170
6 :00		1130		650	6 :00		1170

FEED IW 10:30 AM

FEED OUT 12:10 PM

Day 11:

Feedpot should be at 600 - 650C for priming column.

Reference: Starting-up New Columns, I-PC-09-0108 **Page 6 of 6**

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APPENDIX II RUN-OFF/ UTILITY SHIFT REPORT (EXAMPLES) (INCLUDING LADLE OPERATOR LOGS)

RUN-OFF / UTILITY SHIFT REPORT

DATE: 7-21-10 SHIFT: D (E) N 04

Run-off East: 49
Run-off West:
Utility:

COLUMN#	21	22	23	24	25	26	27	28	1 STRIP	B / #2 strip
RECYCLE/ STRIPPER LADLES	III (3)	X	X	X	X	X	III (3)	III (3)	IIIII IIIII I	X
LIQUATION TEMP.	457 460 457 456		X		X	X	457 453 457 445	456 468 474 476		
IRON DROSS							2830	2705		
LEAD CAST										
CADMIUM CAST		1805								
CYCLONE OXIDE							1830			
BAG FILTER DUST										
OXIDE DROPOUT										
ALL OTHER DROSS							2736 2615	2830 2552		

HC FORM	DOCUMENT NO: F-PC-09-0008	REVISION NO: 2	EFFECTIVE DATE: 04/02/08
DEPARTMENT MANAGER: T. Simon (SOF)		QUALITY MANAGER: T. Beckwith (SOF)	

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RUN-OFF / UTILITY SHIFT REPORT

DATE: 7-21-10 SHIFT: D (E) N 04

Run-off East:
Run-off West: 1041
Utility:

COLUMN#	21	22	23	24	25	26	27	28	A	B / #2 strip
RECYCLE/ STRIPPER LADLES	X	X	5	5 5 1		X	X	X	5 2	4
LIQUATION TEMP.			450 450 / 445 454		524 517 / 523 502				534 538 / 531 532	
IRON DROSS										
LEAD CAST										
CADMIUM CAST										
CYCLONE OXIDE										
BAG FILTER DUST										
OXIDE DROPOUT										
ALL OTHER DROSS										

HC FORM	DOCUMENT NO: F-PC-09-0008	REVISION NO: 2	EFFECTIVE DATE: 04/02/08
DEPARTMENT MANAGER: T. Simon (SOF)		QUALITY MANAGER: T. Beckwith (SOF)	

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RUN-OFF / UTILITY SHIFT REPORT

DATE: 7-21-10 SHIFT: D E (N)

Run-off East: 680
Run-off West:
Utility:

COLUMN#	21	22	23	24	25	26	27	28	A	B / #2 strip
RECYCLE/ STRIPPER LADLES	III (3)	5 5 II 2 (12)					III (3)	II (2)		
LIQUATION TEMP.	454 459 / 450 453						497 497 / 497 495	476 476 / 476 434		
IRON DROSS										
LEAD CAST										
CADMIUM CAST										1200
CYCLONE OXIDE							1680			
BAG FILTER DUST										
OXIDE DROPOUT										
ALL OTHER DROSS	2160-u								1830-d	

HC FORM	DOCUMENT NO: F-PC-09-0008	REVISION NO: 2	EFFECTIVE DATE: 04/02/08
DEPARTMENT MANAGER: T. Simon (SOF)		QUALITY MANAGER: T. Beckwith (SOF)	

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RUN-OFF / UTILITY SHIFT REPORT

DATE: SHIFT: D E (N)

Run-off East:
Run-off West: 28
Utility:

COLUMN#	21	22	23	24	25	~~26~~ 23	27	28	A	B / #2 strip
RECYCLE/ STRIPPER LADLES	X	X	X	卌 I	卌 I	IIII I	X	X	卌 I	卌 II
LIQUATION TEMP.					504 504 / 504 503	449 451 / 450 450			530 529 / 531 530	
IRON DROSS										
LEAD CAST										
CADMIUM CAST										
CYCLONE OXIDE										
BAG FILTER DUST										
OXIDE DROPOUT										
ALL OTHER DROSS										

HC FORM	DOCUMENT NO: F-PC-09-0008	REVISION NO: 2	EFFECTIVE DATE: 04/02/08
DEPARTMENT MANAGER: T. Simon (SOF)		QUALITY MANAGER: T. Beckwith (SOF)	

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RUN-OFF / UTILITY SHIFT REPORT

DATE: 7-22-10 SHIFT (D) E N

Run-off East:
Run-off West: 1308
Utility:

COLUMN#	21	22	(23)	(24)	(25)	26	27	28	(A)	(B) #2 strip
RECYCLE/ STRIPPER LADLES			卌 I	卌 II	卌 II	DOWN			卌 II	卌 IIII
LIQUATION TEMP.			483 480 / 460 484		622 519 / 336 626				547 543 / 543 541	
IRON DROSS										
LEAD CAST					3600					
CADMIUM CAST										750
CYCLONE OXIDE			935				1185			
BAG FILTER DUST										
OXIDE DROPOUT										
ALL OTHER DROSS				T-1985	T-2070 T-2165					13-1600 T-1550

HC FORM	DOCUMENT NO: F-PC-09-0008	REVISION NO: 2	EFFECTIVE DATE: 04/02/08
DEPARTMENT MANAGER: T. Simon (SOF)		QUALITY MANAGER: T. Beckwith (SOF)	

24/25 Lead 1-1700 1900

B-CAD ① 750

East Middle Collector Bay

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RUN-OFF / UTILITY SHIFT REPORT

Run-off East: 461
Run-off West:
Utility:

DATE: 7-22-10 SHIFT: (D) E N 01

COLUMN#	21	22 + STRIP	~~23~~	~~24~~	~~25~~	~~26~~	27	28	~~A~~	~~B / #2 strip~~
RECYCLE/ STRIPPER LADLES	|| (2)	~~||||~~ ~~||||~~ ||||	X	X	X	X	||| (3)	||| (3)	X	X
LIQUATION TEMP.	452 452 / 447 454		X		X	X	470 454 / 449 442	476 453 / 446 456	X	
IRON DROSS										
LEAD CAST										
CADMIUM CAST										
CYCLONE OXIDE										
BAG FILTER DUST										
OXIDE DROPOUT										
ALL OTHER DROSS										

HC FORM	DOCUMENT NO: F-PC-09-0008	REVISION NO: 2	EFFECTIVE DATE: 04/02/08
DEPARTMENT MANAGER: T. Simon (SOF)		QUALITY MANAGER: T. Beckwith (SOF)	

LADLES DUMPED

Clock No's: EAST______ MID. 2345 WEST______ SHIFT: 04 E Date: 7-21-10
Ladles Ordered: ____ Rec'd: ____

Recycle Metal

#21	A Col	#23	#24	#25	#26	#27	#28
|||						|||	|||
Total	Total	Total	Total	Total	Total	Total	Total

#1 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
|	||||					||	|||
Total	Total	Total	Total	Total	Total	Total	Total

#2 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
Total	Total	Total	Total	Total	Total	Total	Total

Furnace Plant

	#22	B
1	330	350
2	420	440
3	500	600
4	535 ~~||~~	625
5	545	730
6	715	830
7	745	900
8	810	930
9	915	1000
10	945	1110
11	1100	
12		
13		
14		
15		
Total		

Cd Tapped ✓

HC FORM F-PC-09-0052, Rev. 4
EFFECTIVE DATE: 04/01/08
Dept. Mgr: T. Simon (SOF)
Quality Mgr: T. Beckwith (SOF)

1 Strip in 24
1 Strip in 25 Per Tom Warnick

HorseheadCSB0004655

LADLES DUMPED

Clock No's: EAST____ MID.____ WEST 620 SHIFT: 04 Date: 7-21
Ladles Ordered:____ Rec'd:____

Recycle Metal

#21	A Col	#23	#24	#25	#26	#27	#28
		II	IIII IIII I	IIII III			
Total	Total	Total	Total	Total	Total	Total	Total

#1 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
Total	Total	Total	Total	Total	Total	Total	Total

#2 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
	I	IIII					
Total	Total	Total	Total	Total	Total	Total	Total

Furnace Plant

	#22	B
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		
Total		

Cd Tapped

HC FORM F-PC-09-0052, Rev. 4
EFFECTIVE DATE: 04/01/08
Dept. Mgr: T. Simon (SOF)
Quality Mgr: T. Beckwith (SOF)

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LADLES DUMPED

Clock No's: EAST C.H. MID. T.J. WEST B.C. SHIFT: N Date: 7.21.10
Ladles Ordered:____ Rec'd:____

Recycle Metal

#21	A Col	#23	#24	#25	#26	#27	#28
II	II					III	II
Total	Total	Total	Total	Total	Total	Total	Total

#1 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
IIII	I					III	IIII
Total	Total	Total	Total	Total	Total	Total	Total

#2 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
Total	Total	Total	Total	Total	Total	Total	Total

Furnace Plant

	#22	B
1	1125	1145
2	1215	1230
3	1250	135 #1
4	140	155
5	210	225
6	235	320
7	255	350
8	335	435
9	405	525
10	455	555
11	510	640
12	540	725
13	610	
14	625	
15	705	
Total		

Cd Tapped 1:15 ✓ 6:20 ✓

HC FORM F-PC-09-0052, Rev. 4
EFFECTIVE DATE: 04/01/08
Dept. Mgr: T. Simon (SOF)
Quality Mgr: T. Beckwith (SOF)

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LADLES DUMPED

Clock No's: EAST______ MID.______ WEST ✓ SHIFT: 02 N Date: 7-21
Ladles Ordered: ____ Rec'd: ____

Recycle Metal

#21	A Col	#23	#24	#25	#26	#27	#28
		|||	~~||||~~ ~~||||~~ |||	~~||||~~ ~~||||~~			
Total	Total	Total	Total	Total	Total	Total	Total

#1 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
Total	Total	Total	Total	Total	Total	Total	Total

#2 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
	||	|||	|				
Total	Total	Total	Total	Total	Total	Total	Total

Furnace Plant

	#22	B
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		
Total		

Cd Tapped

HC FORM F-PC-09-0052, Rev. 4
EFFECTIVE DATE: 04/01/08
Dept. Mgr: T. Simon (SOF)
Quality Mgr: T. Beckwith (SOF)

LADLES DUMPED

Clock No's: EAST 261 MID. KK WEST______ SHIFT: ____ Date: 7-22-10
Ladles Ordered: ____ Rec'd: ____

Recycle Metal

#21	A Col	#23	#24	#25	#26	#27	#28
|	||					||	|||
Total (1)	Total (2)	Total	Total	Total	Total	Total (2)	Total (3)

#1 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
|||	||					||||	||
Total (3)	Total (2)	Total	Total	Total	Total	Total (4)	Total (2)

#2 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
Total	Total	Total	Total	Total	Total	Total	Total

Furnace Plant

	#22	B
1	7:30	8:20
2	#1 7:45	8:50
3	8:30	9:05
4	10:20	9:25
5	10:45	10:35
6	11:15	11:35
7	12:00	12:10
8	12:25	12:40
9	1:45	1:00
10	2:15	2:00
11	#1 3:00	225
12	2:40	255
13	305	320
14		
15		
Total		

Cd Tapped

HC FORM F-PC-09-0052, Rev. 4
EFFECTIVE DATE: 04/01/08
Dept. Mgr: T. Simon (SOF)
Quality Mgr: T. Beckwith (SOF)

LADLES DUMPED

Clock No's: EAST______ MID.______ WEST 125 SHIFT: G1 Date: 7/22/10

Ladles Ordered: ____ Rec'd: ____

Recycle Metal

#21	A Col	#23	#24	#25	#26	#27	#28
Total	Total	Total	Total	Total	Total	Total	Total

#1 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
Total	Total	Total	Total	Total	Total	Total	Total

#2 Strip

#21	A Col	#23	#24	#25	#26	#27	#28
Total	Total	Total	Total	Total	Total	Total	Total

Furnace Plant

#22	B
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	
14	
15	
Total	

Cd Tapped

HC FORM F-PC-09-0052, Rev. 4
EFFECTIVE DATE: 04/01/08
Dept. Mgr: T. Simon (SOF)
Quality Mgr: T. Beckwith (SOF)

HorseheadCSB0004659

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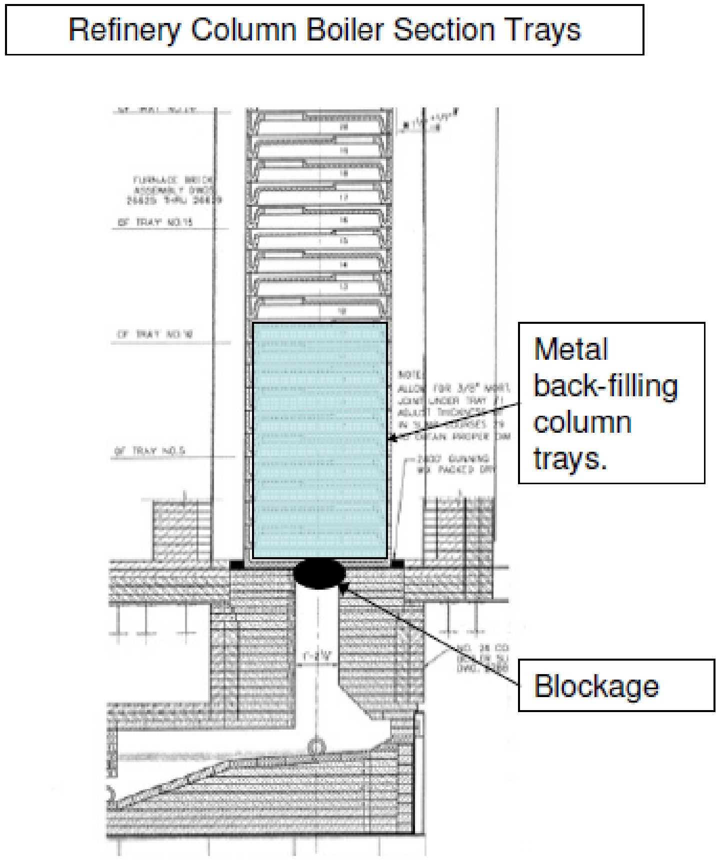
APPENDIX III 2007 REFINERY COLUMN SAFETY SURVEY

Zinc Refinery Safety Survey Feedback May 2007

REFINERY COLUMN SAFETY SURVEY FEEDBACK

INTRODUCTION



In 1993 and 1994, two serious accidents occurred on a zinc refinery in France. Zinc refining was carried out by the distillation of zinc in "New Jersey" zinc refining columns. The main feature of both accidents was the "explosion" of a distillation column when at operating temperature and in normal, continuous operation (not when being warmed). The explosion resulted in a massive eruption of zinc metal and vapour into the workplace. Sadly a number of operating personnel lost their lives.

An investigation of the French accidents identified the cause of both incidents as being the partial blockage of the distillation column sump. Unknown to the operators and their supervision at the time (because some zinc metal was still flowing normally from the sump), the partial blockage was allowing liquid zinc to be held back in the distillation column. Whilst some unusual noises were heard and some vibration was felt, none of the people present linked this to its cause, namely zinc being unable to boil freely in the lower trays of the column. These trays were becoming filled with liquid zinc. Eventually the lower trays failed, resulting in a massive ejection of zinc vapour and boiling metal, which immediately caught fire. The drawing shows a possible example of metal filling the trays as a result of a blockage,

The international enquiry to investigate the accidents revealed that a number of similar incidents had occurred around the world which, whilst not being attributed at the time to backfilling of the column, could have been caused by this. A meeting of a group of operators of the "New Jersey" process in Bristol, UK in October 1994, the purpose being to share experience and knowledge, identified several other accidents or near-accidents caused by partial blockage of the sump and backfilling of the column.

Horsehead Corporation (USA), an attendee of the meeting in Bristol in 1994, decided in 2007 to review its refinery column safety procedures in the light of any knowledge and experience gained since 1994 at zinc refineries using the "New Jersey" distillation process around the world. A survey was sent out. This is a summary of the survey answers and is being sent to all those who have participated. For reasons of confidentiality, this summary does not connect a particular answer with a particular operator.

1

Zinc Refinery Safety Survey Feedback May 2007

SURVEY

PART A – BASIC INFORMATION		
LOCATION OF REFINERY	**Eight refineries were contacted: two responded that they had not operated refining columns for several years and were not able to contribute as most of the people had left the company; one did not respond; five (Chanderiya, Hachinohe, Miasteczko Slaskie, Monaca & Shaoguan) completed the survey.**	
A1 -How many lead refining columns do you operate?	This varied between 2 and 12, total 28.	
A2 -How many cadmium refining columns do you operate?	This varied between 1 and 6, total 14.	
A3 -How many re-boiling columns do you operate?	This varied between 0 and 4, total 6.	
A4 -What is the most common size of column tray?	Almost exclusively (44) of 1372mm x 762mm, but one operator has 4 columns of 1220mm x 610mm.	
PART B – INSTRUMENTATION & CONTROL		
B1 – What is the basic column control mechanism and is it automated? E.g. the fuel flow is fixed, and combustion chamber pressure set point controls recuperator exit damper?	Generally speaking the fuel flow is adjusted and set, and the exit damper is modulated to control the combustion chamber pressure and the oxygen in waste gases. In most cases operation is manual. In the case of two operators the damper position is controlled by the combustion chamber pressure set point, and one further operator has one column only with this automation.	
B2 -Please identify which temperatures you monitor on each column	Feed metal?	All
	Upper Comb. Chamber? 1 or 2?	All have 2
	Middle Comb. Chamber? 1 or 2?	All have 2
	Lower Comb. Chamber? 1 or 2?	All have 2
	Sump Outlet metal?	4 of 5 operators have this (in 1 case not on reboiler).
	Recuperator Inlet? 1 or 2?	3 have 2 points, 2 have 0 points.
	Air Preheat? 1 or 2?	All have this, generally 1 point.
	Recuperator exit? 1 or 2?	All but 1 operator has this – generally 1 point.
	Condenser top?	3 operators have this (1 on column not condenser) and 2 operators do not measure.
	Condenser metal?	3 operators measure this.
	Crossover of Column to Condenser?	1 operator measures this.

2

Zinc Refinery Safety Survey Feedback May 2007

B3 - Please identify which pressures you monitor on each column	Combustion Chamber?	All measure this
	Recuperator exit?	4 operators measure this.
	Condenser?	2 operators measure this (1 not on Cadmium column).
	Exit gas main (e.g. chimney)?	4 operators measure this.
B4 - Please identify which flows you monitor on each column	Fuel (e.g. gas)?	All measure this.
	Feed metal? For example by magnetic inductance?	1 operator measures this.
	Run off metal?	1 operator measures this. 1 operator has observation by video camera on each column.
B5 -Do you monitor or have probes for monitoring any metal levels? E.g. feed box, column sump, condenser sump?	2 operators have probes for metal levels (feed box mainly).	
B6 -Do you measure oxygen levels? E.g. combustion chamber, recuperator exit?	2 operators measure continuously at recuperator exit. 1 of these also takes a monthly manual check at the combustion chamber.	
B7 -Do you measure dust content of each column waste gas?	1 operator measures dust content of each column waste gas. Another operator measures dust content in common exhaust duct.	
B8 - Are the columns mounted on load cells to monitor weight?	1 operator has load cells under each column.	
B9 -Do you monitor column vibrations? If so, in 1, 2, or 3 dimensions?	1 operator monitors vibrations on 3 axes on all columns. Another operator reports testing this but it was abandoned as it did not give useful results.	
B10 -Do you have any special measures to detect column sump blockages and backfilling?	1 operator has probes to detect high level at openings at the back of the column sumps. One operator relies on continuous temperature measurements. It is normal for most operators to physically check flow at regular intervals, and to "flush" column if flow appears too low.	
B11 -Are any of the above of particular use in identifying sump blockages?	Generally operators are not satisfied that they have all desirable means to detect blockages. The operator with the probe at the sump back believes that this is useful and another operator notes that a blockage condition is indicated when there is leakage of metal from around the sump and from the bottom of the combustion chamber and that the bottom trays are dull not bright red colour.	
B12 -Have you ever attempted to develop the capabilities mentioned in questions B4 through B11 above?	1 operator reports developing the blockage clearance technique. Another operator reports unsuccessful vibration monitoring and unsuccessful measurement of pressure in the vertical down-comer using a "bubbler" [this was also tried at Avonmouth].	

3

Zinc Refinery Safety Survey Feedback May 2007

PART C - SAFETY PREVENTION PROCEDURES	
C1 -What is the average training time for column operators?	The answers to this reflect most operators' recognition of the importance of experience in ensuring that the distillation process is safe. Typical answers were "100 hours/person/year"; "1 to 2 years"; "Operators typically have years of experience"; "Average training is 1 year"; "3 months".
C2 -Are there any plant areas where special permission for access is required?	1 operator has no special provisions for this; all the others restrict access to particular parts, notably the combustion chamber area.
C3 -Are the column sumps regularly checked by sweeping (rodding)? How often?	This varies widely from 2 times per shift to 1 time per month.
C4 -Have you ever experienced a blockage of the sump that caused runoff metal to stop flowing? If yes, approximately how many times?	1 operator reports this occurring 5 times in the past 10 years, but only one of these in the past 6 years; 1 operator says "Yes" without specifying further; 1 operator reports a major reduction in frequency since 1999, when feed boxes were enlarged to ensure that dross was trapped better; 1 operator reports "A partial blockage several times per year, but cleared by rodding"; 1 operator reports 3 times, and on one of these the column was shutdown as a precautionary measure.
C5 -Are plant operators aware of the possibility of blockages and backfilling?	All operators report "Yes".
C6 -Do the column sumps have an "open" area at the back where liquid zinc could overflow if the normal front exit was partly blocked?	3 operators report open areas at the back of the sump (1 with the probe); 1 operator reports no open area but a redesign to make rodding easier.
C7 -Are the column combustion chamber walls fitted with "explosion vents" - intentionally weak areas which are designed to fail first in any "explosion"?	2 operators have explosion vents; 1 operator has steel plates positioned in front of combustion chambers to reduce risk to personnel.
C8 -Have any procedures been changed following the French accidents and discussions at that time?	1 operator reports improving control of feed metal flow and combustion chamber temperature; 1 operator reports that the plant was commissioned in 1999 (and took account of what was learnt previously by others); 1 operator reports changing procedures and 1 reports paying more attention to the checking of sumps.

4

Zinc Refinery Safety Survey Feedback May 2007

C9 -Are there any particular safety points that you would mention in connection with the prevention of accidents as a result of blockages and backfilling?	Most of the relevant points are covered above. 1 operator highlights changes to feed box and sump design.
C10 -One of the potential causes for the collection of material (ZnO) that could partially block the sump is the ingress of air to the column. Do you take any special measures to prevent this?	Most operators emphasize the need to prevent air ingress at the feed tube and the sump by ensuring the integrity of baffles, seals etc.
C11 -Do you maintain a minimum rate of run-off flow for each column to minimise the formation of inter-metallic compounds (lead or re-boil column) and to assist with flushing undesirable material away?	All operators maintain a minimum, specified by 1 as 25t/day.
C12 -What is the cross-section size of the vertical outlet hole from the column bottom tray or down-comer?	There is a wide range from 155cm² to 987cm², 2 operators having particularly large areas [which do not appear to be related to reduced blockages at these plants].
C13 -What is the minimum vertical clearance of the underflow for the passage of liquid zinc from the column sump to the run-off exit?	1 operator reports a particularly small dimension (85mm) compared to the others, which are typically 145mm to 200mm.
PART D - DANGEROUS INCIDENTS	
D1 -Please describe any dangerous incidents that have occurred on your zinc refinery in the past 12 years. Were any of these caused by sump blockages and backfilling of the column with liquid zinc? Were any particular lessons learned from these incidents? Were any procedures changed as a result? Was the column design changed as a result?	1 operator reports 2 serious incidents on lead columns in 2000, with partial blocking, no explosion but swelling of the sump due to pressures; due to the clear dangers, the columns were closed down; since then, improvement to feed control has kept blockages to a much lower level. 2 operators report no dangerous incidents. 1 operator reports a catastrophic failure in 1997 as a result of blockage and backfilling; debris included much dross and changes to feed box and sump design have virtually eliminated incidents. 1 operator reports an explosion on a lead column, with no personal injuries and a conclusion that this was caused by blockage and backfilling; several incidents have occurred since then and have resulted in an increase in the vertical clearance in the sump and regular checks on bottom tray colour changes and so on.

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Zinc Refinery Safety Survey Feedback May 2007

D2 –Do you have any particular observations or other remarks to make?	No operators have any particular observations to make.
D3 -Were you aware of the incidents that occurred in France in 1994 prior to receiving this survey?	All operators were aware of the incidents.
Horsehead Industries (Monaca) would like to thank those who completed the survey and hope that this feedback will provide some useful information about what other operators are doing to improve safety in zinc distillation.	

WHH 08-06-07

6

APPENDIX IV COMMENTS ON DRAFT REPORT – HORSEHEAD CORPORATION

ALI ALAVI
Sr. Vice President - Corporate Affairs

4955 STEUBENVILLE PIKE
SUITE 405
PITTSBURGH, PA 15205

WWW.HORSEHEAD.NET
AALAVI@HORSEHEAD.NET

P 724-773-2212
F 412-788-1812
C 412-974-8734

HORSEHEAD CORPORATION
Leading the World in Zinc Recycling

February 20, 2015

Mr. Daniel M. Horowitz, Ph.D.
Managing Director, CSB
2175 K. Street, NW, Ste. 650
Washington, DC 20037-1809

Re: Incident at Horsehead Facility on July 22, 2010

Dear Mr. Horowitz:

Horsehead Corporation ("Horsehead") has had an opportunity to review the draft analysis of the 2010 incident at Horsehead's Monaca, Pennsylvania facility on July 22, 2010 (the "Analysis"). The following sets forth the areas in which Horsehead believes slight corrections and/or revisions should be made prior to any public release of this Analysis.

1. Horsehead disagrees with the opinions and conclusions reached in the Analysis as there is no logical reasoning through the available evidence that can definitively lead to a singular root cause for the July 22, 2010 incident.

2. As a general matter, Horsehead's corporate name is "Horsehead Corporation" and not "Horsehead Holding Corporation." Please make this change wherever necessary in the Analysis. For example, both the Cover Page and the Abstract of the Analysis misidentify Horsehead Corporation as "Horsehead Holding Company" or "Horsehead Holdings". In addition, at page 23, in the first paragraph, the phrase "(Horsehead as it was then)" should be replaced with "(a predecessor to Horsehead)".

3. Mr. William Hunter ("Mr. Hunter") did not visit the Monaca facility while it was in operation, while it was shut down or during cleanup of the July 22, 2010 incident. Mr. Hunter also did not inspect the debris from Column B or any other Column in operation at the Monaca facility, and did not personally interview any Horsehead personnel. Horsehead objects to the Analysis to the extent that it does not clearly set forth this information in **Section I. Introduction (d).**

4. It is Horsehead's understanding that this Analysis purports to be an expert opinion and analysis. As such, Horsehead is concerned with both the language and tone used by Mr. Hunter. Horsehead objects to the Analysis to the extent that it contains Mr. Hunter's personal opinions, rather than his professional opinions and observations or otherwise inflammatory language. The following is a list of instances in which Mr. Hunter interjects inappropriate comments into the Analysis:

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(a) Any reference to "hazardous conditions" being "normalized" should be removed as there are no facts to support this assertion and such inflammatory language is inappropriate in an expert report on the possible causes for the incident at the Monaca facility on July 22, 2010. The information regarding Mr. Hunter's opinion as to the root cause is conveyed without such inflammatory language. The following instances should, therefore, be deleted from the Analysis:

(i) Abstract, page 3, first full paragraph, last sentence.

(ii) Section V. Process Management, last paragraph. This paragraph should be removed in its entirety.

(iii) Section VI. Conclusions, paragraph 12 should be removed in its entirety.

(b) Any comments that are not relevant to the operations at the Monaca facility or do not impact Mr. Hunter's professional analysis of the root cause of the July 22, 2010 incident. The following instances should, therefore, be deleted from the Analysis.

(i) Section II.II, page 10, paragraph beginning "My own experience…" The entire first sentence should be deleted.

(ii) Page 13, the paragraph beginning "The general photographs of the plant are similar to …" should be stricken as irrelevant.

(iii) Any instance of Mr. Hunter's use of exclamation points in the Analysis is inappropriate and should be stricken. *See* pgs. 10, 23.

(iv) On page 11, second paragraph, there is no basis for categorizing past incidents occurring at the Monaca facility as "major incidents." Horsehead objects to this qualifying language and requests that the word "major" be stricken.

(v) Horsehead objects to statements made by Mr. Hunter in which he makes exclamations of surprise or absolute declarations of fact where such declarations are disputed. As a result the following sentence in Section IV.II, page 25, paragraph 4 should be stricken in its entirety: "Given this history, it is surprising that Horsehead management had not put out a general warning that B column was functioning abnormally, that there was a potentially hazardous condition at the sump and that extra care should be taken."

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(vi) Section IV.II, page 25, paragraph 1, should be removed in its entirety. It is not proper for Mr. Hunter to address his "astonishment", reference source material that is not set forth in the Appendix or to ask questions in the body of his analysis.

(vii) Section IV.II, page 26, paragraph 5, to the extent that it contains another inappropriate question in the body of the analysis. The sentence containing the question should be removed.

(viii) Section V. Process Management, last paragraph, last sentence to the extent that it contains another inappropriate and irrelevant question. The entire paragraph should be removed as set forth herein.

(c) As the Analysis purports to be the expert analysis and opinion of Mr. Hunter, Horsehead objects to any instance in which Mr. Hunter's professional opinion is stated as undisputed fact. The following is a list of instances in which Horsehead believes that it should be made clear that the Analysis is Mr. Hunter's professional opinion rather than stated as an undisputed fact:

(i) In the *Abstract at page 3, first full paragraph*: "The physical causes of the accident were..." should begin with "In my professional opinion…"

(ii) In the *Abstract at page 3, last full paragraph:* "The scenario described above..." should begin with "In my professional opinion…"

(iii) In Section IV.I.I, page 16, second bullet, sentence beginning "It was almost certainly too late..." should begin with "In my professional opinion…"

(iv) In Section IV.I.IV, page 21, first bullet, should be revised to make clear that the statements are made in Mr. Hunter's professional opinion.

(v) In Section IV.I.IV, page 22, first bullet, Mr. Hunter uses the language "clearly" to suggest that his opinions are undisputed. Horsehead objects to such a suggestion and requests that the Analysis be revised and each instance of the use of the word "clearly" be replaced with the phrase "in my professional opinion…"

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(vi) In Section IV.II, page 25, paragraph 2, the statement "there was plenty of opportunity for iron levels…" must be revised to state that "there may have been an opportunity for iron levels…" Likewise in paragraph 4, the language "quite clear" should be replaced with "appears".

(vii) Horsehead objects to the entirety of **Section IV.II Analysis of the Data and Causes of the Explosion** to the extent that Mr. Hunter's opinions are stated as undisputed fact rather than qualified by his professional opinion.

(viii) In Section IV.II, page 27, paragraph 10, the language "there is no doubt" should either be stricken or qualified with the language "in my professional opinion..."

(ix) In Section IV.II, page 27, paragraph 12, the language "was almost certainly caused…" should either be stricken or qualified with the language "in my professional opinion..."

(x) Horsehead objects to the entirety of **Section IV.III What Alternatives Scenarios Could Have Caused the Explosion** to the extent that Mr. Hunter's opinions are stated as undisputed fact rather than qualified by his professional opinion. Each paragraph must contain the qualifying language "in my professional opinion..." as Mr. Hunter's analysis is disputed.

(xi) In Section V., page 28, the second sentence is stated as undisputed fact. It should be revised as follows: "However, in my opinion, human factors may have also played a crucial role."

(xii) Horsehead objects to the entirety of **Section VI Conclusions** to the extent that Mr. Hunter's opinions and conclusions are stated as undisputed fact rather than qualified by his professional opinion. Each paragraph must contain the qualifying language "in my professional opinion..." as Mr. Hunter's analysis is disputed.

Horsehead is happy to discuss any of the above comments, corrections and/or revisions at your convenience.

Very truly yours,

APPENDIX V COMMENTS ON DRAFT REPORT – USW LOCAL 8183

Mr. Horowitz,

Thank you for sending me a copy of the report. I really appreciate the CSB for getting to the bottom of the accident. Here are a few comments, I have about the accident.

1. Prior to the accident the employees in that department were always complaining about the sumps being blocked. The Union Safety Committee and Union officials would constantly tell company officials that something needed to be done about the blockage of the sump pumps. The company's response was to put more heat on the sump to melt away the build-up zinc. This did not work. The employees kept on complaining but the company would not listen.
2. When just putting heat on the sumps didn't work the company's solution was to put on heat and stick an air lance in the sump to keep the passage way open. This idea was not working either. The sump kept filling up with hard zinc. The union also complained about this method, but again the company did nothing about it.

After the explosion, the company did make some improvements to the area.

1. They put up wall between the columns.
2. They put in flame guards.
3. Put in explosion doors.
4. Nobody was allowed to go on the floors of 2 and 3. If you went to that level you had to notify the foreman and they would shut down the column.

After the explosion though you still had the same problems with the sumps. The company did nothing to improve in this area. In my opinion, if the company didn't shut down the Monaca facility we probably would have had another column explosion in the future do to not correcting the original problem of the sumps from plugging up.

Thank You,

John Jeffers

President, USW local 8183

WHH 9 March 2015.