EXPERT OPINION OF PAUL B. QUENEAU PAKOOTAS, ET AL. v. TECK COMINCO METALS ET AL. September 15, 2010

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I. INTRODUCTION

My name is Paul B. Queneau. I am President of P. B. Queneau & Associates, Inc. (PBQ & Associates), Principal Metallurgical Engineer at the Bear Group, and an Adjunct Professor in Environmental Science & Engineering at the Colorado School of Mines (CSM).

I was asked to apply my metallurgical education and experience to provide opinions related to known and calculated amounts of effluents from Teck Cominco's Trail smelting complex that entered the Columbia River from 1896 to 2005. These effluents include slag. P. B. Queneau & Associates Inc. (PBQ & Associates) was compensated at a rate of \$300 an hour for my time in preparation of this report. PBQ & Associates was also compensated at the rate of \$200 an hour for time spent by a member of the Bear Group working under my direction on this project.

II. QUALIFICATIONS

I graduated from Cornell University, Ithaca, New York, with a B. Metallurgical Engineering in 1964, and from the University of Minnesota, Minneapolis, Minnesota with a Ph.D. in Metallurgical Engineering in 1967. A copy of my C.V. is attached in Appendix D.

I am a member of the American Institute of Mining, Metallurgical and Petroleum Engineers, The Metallurgical Society (AIME-TMS), the Mining and Metallurgical Society of America (MMSA), and the Canadian Institute of Mining and Metallurgy (CIM). In 2001, I was presented the AIME-TMS Extraction & Processing Distinguished Lecturer Award. I was elected to membership in Tau Beta Pi, and am a Registered Professional Engineer in Colorado. I am a Past President of the Denver Section, Extractive Metallurgy Division of AIME.

For over 20 years I have presented short courses on recycling metals from industrial waste. Locations have included CSM (up to 100 attendees, from many countries; held annually for 18 years), AIME and CIM annual meetings, the U.S. EPA's Office of Solid Waste in Washington, a DOE site and a waste management facility.

Employment History

1997 – Present	President
	P.B. Queneau & Associates, Inc.,
	The Bear Group (Principal Metallurgical Engineer)
	Golden, CO
1990 – Present	Adjunct Professor
	Colorado School of Mines
	Golden, CO
1983 – 1997	Principal Metallurgical Engineer
	Hazen Research, Inc.
	Golden, CO
1982 – 1983	President/Owner
	P. B. Queneau Company, Inc.
	Golden, CO
1972 – 1982	R&D Supervisor
	AMAX, Inc.
	Golden, CO
1967 – 1972	Research Engineer
	Kennecott Copper Corporation
	Salt Lake City, UT

Books

- Meeting Chairman and Editor, <u>Third International Symposium on Recycling</u> <u>Metals and Engineered Materials</u>, Point Clear, Alabama, The Metallurgical Society of AIME, Warrendale, PA (1995).
- Editor, <u>International Symposium on Residues and Effluents Processing</u>, The Metallurgical Society of AIME, Warrendale, PA (1991).
- Editor, <u>Symposium on Arsenic Metallurgy: Fundamentals and Applications</u>, The Metallurgical Society of AIME, Warrendale, PA (1987).

Technical Presentations and Journal Publications

- Recycling Metal-Rich Industrial Byproducts, <u>Nickelhuette Aue 375th</u> <u>Anniversary Celebration</u>, Aue, Germany (2010).
- Rich Country–Rich Wastes: Meeting Needs and Grasping Opportunities, <u>MiMeR/Boliden Foresight Seminar</u>, Lulea, Sweden (2008).

- Recent Developments: Specialty U.S. Metals Recycling Plants, <u>Recycling</u> <u>Metals from Industrial Waste Short Course</u>, Colorado School of Mines, Golden, CO (2008).
- Recycling Zinc in the United States, <u>The El Digest Gathering</u>, San Diego, CA (September 2005).
- Hazardous Waste to Valued Byproducts, <u>The El Digest Gathering</u>, San Diego, CA (September 2004).
- Recycling Non-ferrous Metals from U.S. Industrial Waste, <u>Hydrometallurgy</u> <u>2003</u>, AIME/TMS, 1543-1553 (2003).
- U.S. Plants Operated Solely to Recycle Metal-Rich Secondaries, <u>Extraction</u> <u>and Processing Distinguished Lecturer</u>, AIME/TMS Annual Meeting (2001).
- Recycling Lead and Zinc in the United States, <u>Zinc and Lead Processing</u>, The Metallurgical Society of CIM, 127-153 (1998).
- Production of Copper Chemicals from Secondary and Byproduct Sources in the United States, <u>Journal of Metals</u>, 34-37, 49 (October 1997).
- Production of Byproduct Mercury, <u>Journal of Metals</u>, 24-28 (October 1995).
- State of the Art in Mercury Recycling, <u>Intl. Symp. on Treatment and</u> <u>Minimization of Heavy-Metal Waste</u>, AIME/TMS Annual Meeting, Las Vegas (Feb. 1995).
- Secondary Zinc Production and Waste Minimization, <u>Pollution Engineering</u>, 42-44 (November 1994).
- U.S. Mercury Recyclers Expand Process Capabilities, <u>Hazmat World</u>, 31-34 (February 1994).
- Recycling Lead and Zinc in the United States, <u>4th Intl. Symp. on</u> <u>Hydrometallurgy</u>, Salt Lake City (1993).
- Waste Minimization: Recycling of Spent Lead-acid Batteries, <u>Hazmat World</u>, 34-37 (August 1993).
- Slag Control in Rotary-kiln Incinerators, <u>Pollution Engineering</u>, 26-32 (January 15, 1992).
- Producing Zn/Fe-Based Micronutrient from Copper Flue Dust, <u>Intl. Sym. on</u> <u>Processing Residues and Effluents</u>, San Diego, TMS/AIME, 239-254 (1992).

- Application of Slag Technology to Recycling of Solid Wastes, <u>Intl. Incineration</u> <u>Conf.</u>, Knoxville (1991).
- Optimizing Matte and Slag Composition in Rotary-Furnace Lead Smelting, Intl. Symp. on Primary and Secondary Lead Processing, 145-178, Halifax (1989).
- Processing Petroleum Coke to Recover Vanadium and Nickel, <u>Hydrometallurgy</u>, vol. 22, 3-24 (1989).
- Germanium Recovery at Lang Bay, <u>CIM Bulletin, 79(886)</u>, 92-97 (February 1986).
- Iron Control during Hydrometallurgical Processing of Nickel Laterite Ores, <u>Iron Control in Hydrometallurgy</u>, The Metallurgical Society of CIM, 76-105 (1986).
- Silica in Hydrometallurgy: An Overview, <u>Canadian Metallurgical Quarterly</u>, 25(3), 201-209 (1986).
- Control of Autoclave Scaling during Acid Pressure Leaching of Nickeliferous Laterite, <u>Metallurgical Transactions B of AIME</u>, 433-440 (1984).
- Control of Silica Deposition during Pressure Let-down of Acidic Leach Slurries, <u>Third International Symposium on Hydrometallurgy</u>, 121-137 (1983).
- Soda Ash Digestion of Scheelite, <u>Extr. Metallurgy of Refractory Metals</u>, AIME/TMS, 237-267 (1981).
- Ion Exchange Purification of Ammonium Molybdate Solutions, <u>Hydrometallurgy</u>, vol. 6, 63-73 (1980).
- Fluid-bed Electrolysis of Nickel, <u>Metallurgical Transactions B</u>, 659-666 (December 1979).
- Leaching of Cu/Ni/Fe Matte, <u>Canadian Metallurgical Quarterly</u>, Met. Soc. of CIM, <u>18</u>, 145-153 (1979).
- Nickel/Cobalt Separation by Ozonation, <u>CIM Bulletin</u>, 74-81 (October 1978).
- Leaching of Nickeliferous Limonites, <u>Metallurgical Transactions B of AIME</u>, 547-554 (December 1977).

- Processing WO₃/SnO₂ Concentrate for Brannerite Removal, <u>AIME/SME</u> <u>Metallurgical Trans.</u>, 218-221 (1975).
- Turbine Mixer Fundamentals and Scaleup at Port Nickel, <u>Metallurgical Trans.</u> <u>B of AIME</u>, 149-157 (1975).
- Atmospheric Leaching of Nickel-Copper Matte at Port Nickel, <u>CIM Bulletin</u>, 74-81 (February 1974).
- Nitric Acid Processing of Copper Concentrates, <u>AIME-SME Metallurgical</u> <u>Transactions</u>, 117-123 (June 1973).
- Acid Bake / Leach / Flotation of Molybdenite, <u>Metallurgical Transactions of AIME</u>, 23-27 (November 1971).
- Sulfation of Copper/Iron Sulfides with Concentrated Sulfuric Acid, <u>Journal of</u> <u>Metals</u>, (December 1970).
- Kinetics of Scheelite Dissolution in Alkaline Solutions, <u>Metallurgical Trans.</u> <u>AIME</u>, 2451-59 (November 1969).

Patents

- Autoclave Control during Pressure Oxidation of Molybdenite: <u>U.S. Patent</u> <u>6,818,191</u> (2004).
- Producing Pure MoO₃ from Low-grade Molybdenite Concentrates: <u>U.S.</u> <u>Patent 6,730,279</u> (2004).
- Pickling of Refractory Metals: <u>U.S. Statutory Invention Registration H2087H</u> (2003).
- Inhibiting Lead Leaching in Water: <u>U.S. Patents 5,544,859, 5,632,285 and 6,013,382</u> (1996, 1997, 2000).
- Electrolytic Dissolution and Control of NiS Scale, <u>U.S. Patent 4,627,900</u> (1986).
- Recovery of Alumina Values from Alunite Ore, <u>U.S. Patent 4,618,480</u> (1986).
- Stripping of Tungsten from Organic Solvents, <u>U.S. Patent 4,450,144</u> (1984).
- Recovery of Vanadium and Nickel from Petroleum Coke, <u>U.S. Patent</u> <u>4,443,415</u> (1984).

- Silica Control during Acid Pressure Leaching of Nickel Laterite Ore, <u>U.S.</u> <u>Patent 4,399,109</u> (1983).
- Precipitation of Low-sulfur Calcium Tungstate, <u>U.S. Patent 4,397,821</u> (1983).
- Digestion of Scheelite Concentrates, U.S. Patent 4,351,808 (1982).
- WO₃ Feedback Control when Producing Ammonium Paratungstate, <u>U.S.</u> Patent 4,325,919 (1982).
- Combined Treatment of Wolframite and Scheelite, <u>U.S. Patent 4,320,096</u> (1982).
- Processing of Refractory Tungsten Concentrates, <u>U.S. Patent 4,320,095</u> (1982).
- Upgrading of Scheelite Concentrates, <u>U.S. Patent 4,313,914</u> (1982).
- Separation of SiO₂, P₂O₅ and F from Tungsten Liquors, <u>U.S. Patent</u> <u>4,311,679</u> (1982).
- Separation of Molybdenum from Tungsten, U.S. Patent 4,303,623 (1981).
- Processing Concentrates Having a High MoO₃/WO₃ Ratio, <u>U.S. Patent</u> <u>4,303,622</u> (1981).
- Electrolytic Cell for Oxidation of Ni(OH)₂, <u>U.S. Patent 4,183,792</u> (1980).
- Ion-exchange Process for Recovery of Copper and Nickel, <u>U.S. Patent</u> <u>4,100,043</u> (1978).
- Selective Leaching of Ni/Cu/Fe/S Matte, U.S. Patent 4,094,754 (1978).
- Sulfuric Acid Leaching of Nickeliferous Laterite, U.S. Patent 4,044,096 (1977).
- Separation of Cobalt from Nickel by Ozonation, <u>U.S. Patent 4,034,059</u> (1977).
- High-temperature Neutralization of Nickel Laterite Ores, <u>U.S. Patent</u> <u>3,991,159</u> (1976).
- Atmospheric Leaching of Nickel-Copper-Cobalt Matte Containing Iron, <u>U.S.</u> <u>Patent 3,962,051</u> (1976).
- Selenium Rejection during Acid Leaching of Nickel-Copper Matte, <u>U.S. Patent</u> <u>3,959,097</u> (1976).

- Separating Copper, Lead, and Insol from Molybdenite Concentrates, <u>U.S.</u> <u>Patent 3,834,893</u> (1974).
- Nitric Acid Processing of Chalcopyrite Concentrates, <u>U.S. Patent 3,793,429</u> (1972).

Projects That Involved Zinc and Lead Extractive Metallurgy

- Worked with venture capital firms to evaluate the current capabilities and future potential of U.S. zinc smelters.
- At a zinc monohydrate plant, improved leach circuit operation, and the quality of copper and cadmium cementation byproducts, then converted the leady leach residue to a commercial product.
- Prepared a summary of U.S., Canadian and Mexican steel-mill outputs of electric arc furnace (EAF) dust; detailed alternative methods in use for recovering zinc therefrom; and worked with client to implement dust processing improvements.
- Evaluated alternative methods for zinc recovery from a manganese-rich silver ore, including assessing production of electrowon metal vs micronutrient.
- Physical and thermal processing of spent alkaline batteries to recover zinc oxide fume and a iron-manganese calcine.
- Evaluated primary zinc plant (roast/leach/electrowin) as an acquisition candidate for processing sphalerite concentrate output from proposed mine/concentrator.
- Worked with operating management to improve yield at a plant recovering zinc slab, zinc granules, and micronutrient fines from skimmings.
- Developed technical and marketing criteria to profitably recover zinc-iron sulfate micronutrient from secondary copper smelter dust.
- Studied alternative raw materials and technologies for preparing zinc oxide and hydroxide secondaries to be processed by leaching and purification, followed by electrowinning.
- Provided technical support and economic evaluation for a power plant preparing to produce ZnO byproduct recovered from combustion of tires. Worked with a second power plant to improve zinc recovery.

- Worked with EPA contractor to assemble "a guide on recycling low-metalcontent wastes for use by decision makers at superfund, RCRA, and other waste sites."
- Prepared secondary-lead-plant operating criteria for the International Lead Management Center for third-world plant, including a leach circuit for desulfurizing the reverberatory furnace feed.
- Worked with a major U.S. chemical manufacturer and North American secondary lead smelters to process sludge and soil contaminated with tetraethyl lead.
- Assisted a lead-acid battery recycler with blast furnace formulations to maximize slag environmental acceptability without significantly affecting production efficiency.
- Assisted in developing method to minimize lead transfer into tap water. Our modified procedure for manufacturing bronze valves was then implemented by a major water-valve producer.
- Established means to predictably integrate diverse waste byproducts from lead chemical production into a spent lead-acid-battery rotary-furnace operation.
- Developed a slag solidification procedure to minimize concentration of cadmium and lead reporting to the leachate in the EPA's TCLP procedure.
- Upgraded operating practices of furnaces converting drosses to Sn-Pb solder, resulting in the doubling of furnace output while improving yield by over 20%.

III. CASES IN WHICH PAUL B. QUENEAU TESTIFIED AS AN EXPERT AT TRIAL OR BY DEPOSITION DURING THE PAST FOUR YEARS

During the past four years, Paul B. Queneau has testified as an expert witness at trial or by deposition in one case:

<u>PERINE v. E.I. DUPONT ET AL., 2007</u>: I was asked to apply my metallurgical education and experience to provide opinions related to zinc production at Spelter, WV, between 1911 and when secondary operations ceased in the early 2000s.

IV. BASES AND SUPPORTING INFORMATION

The opinions contained in the report are based on 43 years of experience as a practicing extractive metallurgist, and 20 years as an Adjunct Professor in the Department of Environmental Science and Engineering at the Colorado School of Mines. In addition to my personal experience I have examined, at least briefly, the technical papers, books, and documents listed in Appendix C.

V. THE PURPOSE OF THIS REPORT

The issue addressed in this expert report is the direct discharge of metalcontaining effluents from Trail's metallurgical facilities, primarily into the Columbia River. Focus is on the evolution of the processes and operations related to lead, zinc, and copper smelting and refining. Included are the following:

- Changes in the processes and operations, particularly relating to the character and quantity of solid and liquid wastes.
- Disposition of Trail unit operation intermediates and outputs, including those from furnaces and kettles, dust and fume treatment, acid plants, zinc leaching and purification, lead and zinc tankhouses, and byproduct recovery.¹
- Disposal practices over time.
- Feedstocks used in the various operations and the resulting variations in solid and liquid wastes; plus the impact, if any, of changes to feedstock used in various processes on the character and quantity of wastes.
- Types, origins, compositions, and quantities of solid and liquid wastes discharged by Trail metallurgical operations to the Columbia River over time.
- Air emissions from Trail operations were addressed in order to calculate yearby-year material balances, specifically for lead, zinc, arsenic, cadmium, and mercury.

¹ A Glossary of Terms can be found in Appendix B.

VI. EXECUTIVE SUMMARY

Slag is a byproduct of high-temperature recovery of metals. In the context of this report, slag is a glass-like material consisting primarily of silica, lime and iron (oxide and metallic), as well as small amounts of base metals, including zinc, lead, copper, arsenic, and cadmium.

Details on direct slag and metal discharges, primarily to the Columbia River, are tabulated in Tables 2 and 3, Section XVI – *Inputs and Distributions Spreadsheets*. Estimates are provided of the weight of Pb, Zn, As, Cd and Hg originating from Trail's metallurgical operations from 1921 to 2005 that discharged directly into either the Columbia River or into Stoney Creek.

These discharge totals do not include all of Pb, Zn, As, Cd, and Hg discharged into the Columbia and Stoney Creek from Trail operations, specifically not:

- Spills of process fluids and slurries, e.g., the 7.7 tons of mercury and 10 tons of zinc discharged into the Columbia River on April 23, 1981 (Cominco, 2007, TECK 0058576).
- Storm water drainage (Cominco, 2007, 005877), and contaminated effluent from groundwater, e.g., seepage along the banks of Stoney Creek and other plant properties (Cominco, 2007, 005877).
- Discharges originating from non-metallurgical sources, e.g., the mercury content of phosphate rock that was leached with Trail's sulfuric acid output to produce fertilizer (1930 1993).
- The contribution of Pb, Zn, As, Cd, and Hg from atmospheric discharges from Trail that found a path to the Columbia River.
- Emissions from coal burning.

A. Lead Slag Discharges (1921 to 1997)

- Lead slag discharged to the Columbia: 13,300,000 tons
- Lead in lead slag discharged to the Columbia: 45,700 tons
- Zinc in lead slag discharged to the Columbia: 479,000 tons
- Arsenic in lead slag discharged to the Columbia: 2,840 tons
- Cadmium in lead slag discharged to the Columbia: 193 tons
- Mercury in lead slag discharged to the Columbia: Nil

B. Non-Slag Discharges (1921 to 2005)

- Non-slag lead to the Columbia: 22,300 tons
- Non-slag zinc, primarily to the Columbia: 284,000 tons
- Non-slag arsenic to the Columbia: 677 tons
- Non-slag cadmium to the Columbia: 972 tons
- Non-slag mercury, primarily to the Columbia: 227 tons²

VII. TRAIL OPERATIONS IN ONE PARAGRAPH

The Trail metal and fertilizer production facilities are located approximately 10 river miles upstream from the U.S.-Canada border in Trail, B.C., Canada. Smelter operations have been underway in Trail since 1896. The smelter was owned by a company which became known as Consolidated Mining and Smelting Company of Canada, Ltd., in 1906, was officially renamed Cominco in 1966, and merged with Teck Ltd. to become Teck Cominco Metals, Ltd., in 2001. The facility primarily produced precious metals, copper, lead, and silver during the first decade of operation. Zinc production was initiated in 1916. Plants for production of nitrogen- and phosphorus-based fertilizers began operations in 1930. Although the smelter was originally built to process materials from local mines, it currently processes ore concentrates obtained from mining operations throughout the world. In addition to lead, zinc, cadmium, silver, gold, bismuth, antimony, indium, germanium, arsenic, and mercury, Trail also produces sulfuric acid, liquid sulfur dioxide, and elemental sulfur.

VIII. AN OVERVIEW OF METAL AND METAL-CONTAINING BYPRODUCT PRODUCTION AT TRAIL

To quantify smelter- and refinery-derived effluents that subsequently discharged primarily to the Columbia River via Trail's sewers, it is helpful to understand the processes that created these discharges. This write-up therefore describes the various hydrometallurgical and pyrometallurgical steps that evolved at Trail over 109 years of operation.

A century provides ample opportunity for production, innovation, and change. Change at Trail was particularly rapid between 1896 and 1936, and between

² This report uses short tons (2000 lb), unless specified otherwise.

> 1980 and 2000. Focus was on production of base and precious metals. Byproduct fertilizer operations productively utilized important portions of smelter and refinery effluents; aspects of this nearby facility are also detailed.

A. Stages of Growth at Trail: 1896 to 1995

Briefly tabulated below are key steps in the growth of Trail operations from a 19th Century tent camp to one of the 21st Century's major metal producers.

Overview: The Teck Cominco smelter was originally built by Fritz August Heinze on a bluff above the Columbia River in British Columbia, Canada. He was the driving force behind construction and start-up of the copper smelter in 1895-6 (Fish / Cominco, p 92, 1997). Mr. Heinze had been head of the smelting works in Butte, Montana, and thus brought the expertise to treat the Rossland copper-gold ores. Most of the ores' dollar value was in the gold. It was Heinze who obtained a land grant at Trail from the Dominion Government, founding the British Columbia Smelting & Refining Company.

Location of the Trail smelter: In 1896, Heinze sited his smelter about 120 feet above the Columbia. A later reference (Turnbull, 1907, p 421) states that the smelter was located on the edge of a flat sand bench that rose about 200 feet directly above the Columbia at the junction of Trail Creek. See Figure 1.



Figure 1. Trail Creek in 1896 – Rails and ties are being unloaded from the Columbia and Western Railway work train (Trail Historical Society – Photo # 1829)

When establishing a location for a smelter, where to put the slag is an important consideration. One attempts to anticipate what the future will bring. J.E. Johnson, a prominent engineer and author in the field of iron blast-furnace construction and practice, observed in 1917 that: *It is not always easy to find a place in which to dispose of the slag without a long chance that one will later on be exceedingly sorry for having put it there* (pp 351-352). Johnson then describes ongoing use of slag granulation at Iron Gate, Virginia, followed by flushing the slag granules into the James River to be carried away by the current.

In regard to slag waste, substantial savings can be derived by water granulation of the molten slag, then using water to sweep slag to its dumping location. This procedure is substantially more economic than mechanically transporting the slag. Additional savings can be attained by discarding the slag into a river, rather than preparing and maintaining a slag dumping ground (Surface Arrangements, Textbook, 1902, pp 42-44).

By 1926, it was clear to Donald M. Liddell (Managing Editor of *The Engineering and Mining Journal*; Secretary of the Mining and Metallurgical Society of America) that an important smelter siting consideration involved anticipating the path of toxic liquid and solid wastes dispersed downstream / downwind from the plant (Vol 1, p 603). Unless means were implemented to avoid the associated damage, lawsuits could result.

Plants which have a waste disposal containing cyanide or other harmful or poisonous ingredients must consider the people and livestock on the downstream side of the mill, or suits may arise involving damage and riparian rights. Plants which emit obnoxious fumes must guard against smoke suits. This can be done either by installing expensive mechanical and chemical means of rendering the gases innocuous, or by constructing the plant of such type and in such localities that the fumes will be so diluted and disseminated before they reach any land capable of producing crops that the danger of smoke suits may be eliminated.

During the 1930s and 1940s, there was a Trail Smelter Arbitration. This arbitration addressed complaints from American farmers located downwind.

In 1936, S.W Griffin and E.F. Potter completed a study for the Bureau of Chemistry and Soils at the U.S. Department of Agriculture: *Undissolved Mineral Matter, Natural and Extraneous, in the Columbia River in Northern Stevens County, Washington: Slag Pollution.* The final paragraph (p 98) of this report reads:

It is recommended that all smelter wastes be excluded from the Columbia River, – and in particular it is suggested that officials of the Trail Smelter be asked to cause the abatement, at their plant, of the nuisance of slag-pollution of the river.

In 1943, Trail management gave considerable thought to building a new smelter at a new site. However, key process operations already in place were relatively modern. The transfer of materials to and from other departments by pipeline also influenced the decision to rebuild within the existing boundaries. These legacy operations were thus *effective anchors to the old site* (Anonymous, <u>Canadian Mining Journal</u>, 1954, p 234).

Trail also completed a detailed study (about 1975) of the possibility of making a large investment in another site in Canada. The company determined that the advantages at Trail far outweighed disadvantages. The roasters, acid plants, lead refinery, the electrical power supply, shops and services, and the community infrastructure at Trail were all deciding factors in maintaining a complete smelting operation at Trail (Fish / Cominco, 1981, p 48).

In 1898, Heinze sold his holdings to the Canadian Pacific Railroad, which renamed the facility Canadian Smelting Works. The new owners immediately enlarged plant capacity. By 1901, management had created a lead smelting department.

Copper ore feedstock and copper matte product: The Columbia and Western Railroad delivered most of the smelter's ore from Rossland, an eleven-mile trip with switchbacks to overcome the 2100-foot drop in elevation. About seven tons/day (tons per day; tpd) of low-grade copper matte product were shipped to Butte, Montana. Matte is a mixture of metallic sulfides. In copper smelting, it is a mixture of copper (Cu) and iron sulfide. In subsequent years, Trail roasted (burnt) this matte, then smelted (melted and processed) the roasted output to produce high-grade matte (40% Cu).

Roasting to remove sulfur: Roasting (or calcining) of the ore rejected sulfur as sulfur dioxide gas (SO₂). The calcine contained most of the metal oxides. Sufficient sulfide remained in the calcine to permit formation of copper-iron matte during subsequent smelting. In the beginning, ore and limestone were piled up along with wood and set on fire (Fish, 1997, p 92; Cominco, 2007, TECK 0058560). In less than a year, the heaps were replaced by more efficient mechanical roasters (Carlyle, Provincial Geologist, 1896, p 18).

Production of sulfuric acid from roaster offgas: Beginning in 1916-17, Trail produced 30 tpd of sulfuric acid from zinc roaster gas in two small chamber plants. Outside sources of acid were both unreliable and expensive. A third acid plant, this one using a modified Grillo process, came on line in 1929 (35 tpd). In 1931, three additional units came on line, each rated at 112 tpd acid (King / Cominco, 1950, p 2243). Over a third of the SO₂ released by roasting was then being captured for production and utilization of sulfuric acid.

In 1936, a portion of the roaster offgas was diverted to produce 100% SO₂, which was used to enrich dilute lead sinter-plant offgas. The SO₂ generated during sintering was then captured. In 1938, two additional sulfuric acid plants came on line, which increased Trail's rated capacity of installed units to 600 tons sulfuric acid per day (100% H_2SO_4 basis). Acid production required thorough scrubbing of sinter-plant and roaster offgas. This scrubbing captured metal values that now became available for disposal to the Columbia River (King / Cominco, 1950, p 2243).

Copper smelting to produce matte product and slag waste: Good roasting practice minimizes formation of liquid phase. In contrast, smelting produces liquid phases, e.g., a heavy matte and a lighter (less dense) fluid slag that floats on top of the matte. Slag is predominantly a mixture of metal oxides that have a relatively low affinity for sulfur. Slag and matte are tapped (removed from the furnace) separately. Copper slag is rich in the silicates of oxygen-loving elements, such as iron (Fe), calcium (Ca), magnesium (Mg), and aluminum (Al). The slag's copper content is relatively low, because copper prefers to be associated with sulfur rather than oxygen. Precious metals dissolve in the matte.

In 1896, Trail operated one blast furnace (BF: a vertical smelting furnace) and four reverberatory furnaces (RVFs: horizontal smelting furnaces). By 1898, three 600-ton per day blast furnaces and 48 enclosed roasters had been installed. Fuel and reductant were principally wood (sourced locally), coal, and coke (coal that has been heated to remove volatile constituents). Coal from the U.S. Rocky Mountains was imported via rail to the Columbia River, then sent downstream to Trail in scows. Coke was imported from Fairhaven, Washington. Reductants are substances that can remove oxygen, in this case to assist in formation of Cu_2S -FeS matte product for shipment to Butte.

Trail's early slags from copper production assayed 42 to 46% silica (SiO₂), 12 to 19% FeO, 14 to 19% alumina (Al_2O_3), and 4 to 6% magnesia (MgO); see

Carlyle, 1896, p 19. This slag was tapped from the furnaces into gutters and slag pots, from which the slag was discharged down the side of the bluff above the Columbia River. The bluff slopes were thus protected against erosion.

The bluff on which the smelter stands is sand, but the top and face of the dump, 120 feet high, are being covered with slag that flows in sand gutters from the reverberatories, or is wheeled out in the usual slag-pots from the blast furnace.

Plans called for granulating the slag, then sweeping it out to the dump (Carlyle, 1896, p 19). As time passed, the bluff gradually extended outward with *a mixture of granulated slag, gravel, ashes, and general refuse* (Murray / CM&S, 1933, p 85). By 1907, slag generated during copper smelting was being water granulated (Turnbull, 1907, p 424). Two lead blast furnaces were also in operation (Turnbull, 1907, p 421). Trail's slag output during this period would thus have been from both lead and copper smelting. The slag generated during lead smelting was most likely also granulated.

Figure 2 shows the Trail smelter in 1896, with the embankment below extending to near the Columbia River's edge (B.C. Archives). A riverbank retaining wall was built in 1921, then extended in 1922, to hold slag from copper and lead smelting in place. This wall was 37 to 50 feet high (Murray / CM&S, 1933, p 87).

Figure 3, a photo taken in about 1930 during construction of the slag fuming plant, shows this wall. Slag, which must have been produced by Trail's copper and lead smelting operations, appears to have built up behind and above the retaining wall, then cascaded into the Columbia River. Note that the buildings below the bluff to the left in Figure 2 are also shown in Figure 1.



1894

Figure 2. View of the Trail copper smelter in 1896, showing the close proximity to the Columbia River (B.C. Archives)



Figure 3. View of Trail's BF slag fuming plant under construction in about 1930; shown is a retaining wall below the plant along the Columbia that held back slag, gravel, ashes, and general refuse (Murray / CM&S, 1933, p 85) **Handling furnace offgas**: Until the installation of hot Cottrell electrostatic precipitators in 1914, smoke from the furnaces was cooled, then passed through dust settling chambers that fed a chimney. Fine dust swept up the stack was likely enriched in arsenic (As) and cadmium (Cd). The basis for this conclusion is as follows:

- Arsenic and Cd and their oxides and chlorides are easily volatilized.
- A significant portion of the As and Cd condenses on dust surfaces.
- Most of this surface is associated with the finer dust fractions.
- Fine dust settles slowly, and thus more readily passes through settling chambers into the stack, then to the atmosphere.

A portion of the As and Cd, as well as most of the mercury (Hg), does not condense. This uncondensed fraction is swept up the stack as fume.

Production of lead: Trail operations roasted and smelted lead sulfide ores and concentrates beginning in 1899 (McNab, 1909, p 424). A second historical account states that the decision to include lead smelting at Trail was made in 1901 (Cominco, 2007, TECK 0058560). Roasted feedstocks were smelted in a blast furnace (BF) to produce lead bullion product. A blast furnace is a shaft down which agglomerated lead-rich oxides are reduced to lead using carbon (coke) to produce liquid lead bullion, slag, plus offgas carrying dust, carbon monoxide, and fume. Small quantities of speiss (e.g., iron-rich arsenide) and matte are also formed. Precious metals transfer into the lead bullion.

By 1902, Trail commissioned the world's first electrolytic lead plant; see Figure 4 (Fish, 1997, p 93). This operation, the Betts electrolytic process, refined (purified) blast-furnace lead (Pb). Betts electrorefining continues, expanded and modernized, at Trail as of the date of this report.

<u>Acquisition of key mines</u>: Mines purchased by Trail in 1905-06 included the Rossland and St. Eugene. To reflect this expansion, the company was renamed *The Consolidated Mining and Smelting Company of Canada Limited* (CM&S). This name remained until it was changed to *Cominco* in 1966.



Figure 4. Interior view of the early Betts electrolytic refinery showing the arrangement of the cells (Fish, 1997, p 93)

Most important to Trail's future was purchase of the Sullivan Mine in 1913. By 1914, the Sullivan became the largest lead producer in Canada. After commercialization of sulfide flotation to separate zinc (Zn) sulfide from lead (Pb) sulfide, this mine also became a world-class zinc producer. Output was high-grade lead concentrate, and high-grade zinc concentrate. After 92 years of operation, the Sullivan mine was closed in 2001. Ore mined from the Sullivan contained approximately 9 million tons of lead, 8 million tons of zinc, and 285 million ounces of silver. (Horswill, Northern Miner, Nov 5, 2001).

In addition to the Sullivan, the Pine Point and Red Dog mines were / are the principal source of zinc and lead concentrates fed to Trail's metallurgical operations. The Pine Point mine (Northwest Territories in Canada; owned by Cominco) produced lead and zinc concentrates from 1964 to 1988; the zinc concentrate was consumed at Trail. This concentrate contained minimal amounts of detrimental impurities (Giroux, 2001, p 21). The Red Dog mine (Alaska; owned by Teck Metals) began production in December 1989. A major portion of both Red Dog's zinc and lead concentrate output are shipped to Trail.

Our best estimates of the metal content of typical Sullivan, Pine Point, and Red Dog concentrates consumed at Trail appear in Table I. See the attached *Inputs and Distributions* spreadsheets for details on the sources from which these assays were obtained.

				Arsenic,		Hg, ppm
	Lead, %	Zinc, %	Cadmium, %	%	Cu, %	
Lead Concentrat	e					
Sullivan	57.2 - 71.0	3.7 - 11.9	0.017 - 0.020	0.03 - 0.04	0.12	10
Red Dog	55.0 - 62.5	10.0 - 10.8	0.01 - 0.12	0.04 - 0.07	0.06	18
Zinc Concentrate	9					
Sullivan Pine	3.5 - 7.2	36.2 - 53.3	0.13 - 0.18	0.024	0.15	60
Point	1.4 - 2.1	56.7 - 59.3	0.10	0.025	0.03	20
Red Dog	3.2	54.8 - 57.0	0.33	0.02	0.14	94 - 104

TABLE 1. TRAIL FEED CONCENTRATE ANALYSES³

Production of electrolytic zinc and copper (1916): Trail's electrolytic zinc and copper refineries came on line in 1916 (Fish, 1997, p 94). Incentives included war-time need for cartridge brass (an alloy of Cu and Zn), as well as minimizing product shipping and refining cost. Copper smelting and refining at Trail ceased in 1930 due to a shortage of economic feedstocks. Electrolytic zinc output in 1916 was 30 short tons/day, which had increased to 325 stpd by 1930, and to 450 stpd by 1948. Expanded and modernized zinc tankhouse operation continues at Trail to this day. Refined zinc output from Trail in 2006 was 725 stpd.

<u>Separation of lead from zinc by flotation (1923)</u>: Key to large-scale production of zinc by electrolysis was Trail's development of sulfide flotation to produce separate lead and zinc concentrates. Hand sorting (Figure 5) was displaced by flotation (Figure 6). The Sullivan Concentrator at Kimberly using differential flotation commenced operation in August, 1923.

 $^{^3}$ The thallium content of Sullivan lead concentrate is about 340 ppm (NRC assay, 2008, p 2). PBQ – Expert Opinion - 9/15/10



Figure 5. Hand sorting to separate lead and zinc minerals at the Sullivan mine (Fish, 1997, p 94)

Selective flotation also minimized subsequent interference from zinc in the lead smelter, because Sullivan lead flotation concentrate was relatively low in zinc content, e.g., 66% Pb and 6% Zn. Conversely, Sullivan zinc flotation concentrate was relatively low in lead content, e.g., 44% Zn and 5.3% Pb. Calcining and leaching this zinc concentrate generated zinc-rich solution, plus lead-rich zinc-poor leach residue. This residue was blended with lead-rich feedstock in preparation for sintering prior to blast-furnace reduction.



Figure 6. Early wooden flotation cells used to produce separate lead and zinc sulfide concentrates (Fish, 1997, p 94)

Fuming of lead blast furnace slag (1930): Prior to development of the Sullivan mine, Trail's lead BF slags were reasonably low in zinc content, i.e., 7 to 12% Zn (McNab, 1909, p 431). Once Sullivan output became significant, so did the zinc content of the lead BF slag. By 1920, Trail had began accumulating lead BF slag (15 to 20% Zn) in large stockpiles in anticipation of inventing a means to recover this zinc (Yurko / Cominco, 1970, p 331). Zinc built up rapidly in the lead BF slag; flotation separation of lead from zinc had not yet been commercialized. In 1924, the Staff of CM&S wrote that a considerable tonnage of this slag [high iron and zinc] has been stored with a view to recovering the zinc (p 455).

Even after lead-zinc flotation separation came on line, the zinc content of lead BF slag remained high. The operators simply fed more lead to the BF until the 15 to 20% Zn slag limitation was met. Zinc-rich BF slag inventory thus accumulated during the 1920s. Meanwhile, Trail's research staff worked to develop an economic process to recover this zinc.

Research succeeded in 1929. The installation of BF slag fuming in 1930 enabled about 85% of the zinc, and almost all of the residual lead, to be recovered from the zinc-rich lead BF slag. Blowing air and coal fines into the molten BF slag fumed (volatilized) the zinc, residual lead, and a substantial portion of the cadmium, arsenic, and indium. Product fume was then oxidized and condensed as flue dust, which was captured in baghouses for recovery of metal values. Granulating and discarding the fumed slag into the Columbia River (typically <0.1% Pb and <5% Zn) completed the process.

Analysis of the fumed slag remained steady at about 2.5% Zn and 0.1% Pb; iron, silica, lime, and copper content were 31%, 30%, 17%, and 0.3%, respectively (Fish, 1981, p 55). Cominco subsequently provided this assay as typical for fumed slag (Cominco, 1985, TECK 0617708, p 37). Discharge of fumed slag into the Columbia River continued until 1995.

For Trail's annual lead BF slag, fumed slag, and refined lead production, I relied on the values that Teck provided; see TECK 0715785. Slag outputs were calculated by Cominco from 1910 through 1997. To check these numbers, I relied on smelter data provided in Trail's published technical articles. Using these inputs, slag tonnages were calculated for ten individual years between 1913 and 1990 (i.e., due diligence, picking years for which there was sufficient data). Slag tonnage outputs from these calculations were reasonably consistent with those provided by Teck. Furthermore, the

Cominco's calculated slag tonnages are reasonably close to those appearing in the company's technical articles.

Cominco also provided a tabulation of the annual quantity of lead slag discharged to the Columbia River (Teck 0715785); no lead slag is shown going into the river from 1910 to 1920. That slag did not reach the Columbia during this period appears unlikely. Based on examination of Figure 2, if slag had not already reached the Columbia River in 1896, it likely would have done so by the end of the century. Until a retaining wall was built in 1921, the slag likely continued to enter the river.

Furthermore, the quantity of slag shown by Cominco as going to the Columbia from 1920 to 1929 (Teck 0715785) appears to be much higher than it should be. High-zinc slag was produced and inventoried during this period. Only after zinc values were fumed from this slag inventory beginning in 1930 was the slag regranulated, then delivered to the Columbia River. For details, refer back to the discussion above on stockpiling zinc-rich slag. Also see Section X-A below: Specifics on the Early Years of Lead Operations; e.g., *...some 500,000 tons of old slag, running about 20% Zn, has been accumulated* (Mason / Cominco, 1929, p 342).

Production of fertilizer from Trail byproducts (1931): In 1930, CM&S constructed a chemical complex to manufacture fertilizer at Warfield Flat, a terrace located above the smelter. The company built this plant in anticipation of receiving a key raw material – sulfuric acid – from Trail.

Beginning in 1931, about 38% of the sulfur that had been released to the atmosphere at Trail was converted to sulfuric acid. This acid, derived from the sulfur dioxide gas (SO₂) produced when roasting zinc sulfide concentrates, was in turn converted to commercial fertilizer products. By 1948, 90% of the sulfur in Trail feedstocks was being converted to sulfuric acid.

There was substantial synergy between smelter and fertilizer operations:

- <u>Steam</u> generated during roasting of zinc concentrate was utilized during evaporation of fertilizer solution.
- <u>Oxygen</u> byproduct from fertilizer production was consumed when used to improve smelting and roasting efficiency.
- <u>Ammonia solution</u> from fertilizer production was used to scrub dilute smelter offgases, which in turn produced additional fertilizer.

- <u>Zinc micronutrient fertilizer</u> was later produced from a portion of the zinc sulfate electrolyte purged from the tankhouse.
- <u>Fluosilicic acid</u> byproduct from leaching phosphate rock was captured for use as an electrolyte additive in lead electrolytic refining; it was therefore no longer necessary to react sulfuric acid with calcium fluoride to produce hydrofluosilicic acid.

Suspension roasting of zinc sulfide concentrates (1936): Offgas from roasting and sintering (agglomerating) lead BF feedstock was too dilute to economically produce sulfuric acid. In contrast, offgas from roasting zinc sulfide (ZnS) concentrate contained higher and more controllable concentrations of SO₂.

Therefore in 1936 Trail targeted its ZnS roasting process to maximize sulfuric acid output and economics. The company provided additional space between roaster hearths to facilitate sulfide particle combustion while in free fall. A portion of the nitrogen in the furnace combustion air was then replaced with oxygen delivered from Trail's uphill fertilizer operation. The result was output of 6 to 8% SO₂ roaster offgas from which sulfuric acid was efficiently manufactured.

Upgrading zinc concentrate roaster operations opened the door for additional economic recovery of sulfuric acid.

<u>Minimizing loss of lead tankhouse electroyte</u>: In the early years, loss of lead fluosilicate electrolyte solution provided sufficient purge from the lead tankhouse to control impurity concentration. However, by the mid-1930s tankhouse operation had become so efficient that it became necessary to withdraw electrolyte from the system. This purge was treated to recover a substantial portion of its lead and fluosilicic acid content (Fingland, 1930, p 190).

Establishing a major source of captive electric power (1942): To meet ever-increasing needs for power, CM&S in 1942 put the Brilliant Dam into operation on the Kootenay River. By 1948, more power was consumed in Trail than in all of the rest of British Columbia.

<u>Support of World War II efforts</u>: Trail's fertilizer plant commenced production of explosive-grade ammonium nitrate at Warfield (2 miles west of downtown Trail) and Calgary, at the request of the Canadian government.

This facility was operated on a no-fee basis. CM&S also worked with the American government to build a secret heavy-water plant at Warfield to support early experiments in nuclear fusion (Figure 7), which operated from 1944 to 1955 (Cominco, 2007, TECK 0058563).



Figure 7. The secret heavy water plant at Trail that was one of Cominco's many war-time contributions (Fish, 1997, p 95)

Recovering dust and fume from furnace offgas: Until 1914, the primary means to minimize dust and fume (volatilized metals) loss to atmosphere was by cooling and settling. In 1914-15, Cottrell electrostatic precipitators were installed to substantially improve fume and dust recovery for lead blast roasting (to agglomerate the BF feed), the lead blast furnaces, and copper converting (Hoffman, pp 457-458, 1918). By 1931, hot Cottrells were in service for the sintering machines, zinc roasters, acid plant, and silver refinery.

More complete dust collection was then attained by installing baghouses following slag fuming (1930), the silver refinery (1939), lead blast furnace smelting (1951), the antimonial lead plant, and zinc roasting (1962). Cadmium-rich dust collected in the lead BF baghouse was pneumatically pumped to the slag fuming operation. Fuming of this dust provided the major purge of cadmium from the smelter (Fish, 1981, p 57). A portion of the arsenic was also purged.

Minor metal recovery: A key to minimizing metal outfall is maximizing recovery. The years in which recovery of key minor metals began are as follows: cadmium (1927), bismuth metal (1929), antimony (1938), indium (1941), arsenic as lead-arsenic-antimony alloy (by 1973), high-purity arsenic metal (1974), mercury (1981), and copper arsenate (1989). Gold and silver were recovered from the beginning (1896), not only because of their value, but also because these noble elements follow copper and lead during smelting.

<u>The modernization of Trail</u>: The major modernization of Trail began in 1979-89 with installation of continuous drossing of the lead bullion, construction of a modern lead-smelter feed plant, and upgrading of the roaster oxide leach plant. Numerous other upgrades followed, the primary focus of which was improving plant economics. The environment was not neglected in this modernization. Metallurgical modernization projects that achieved major effluent reductions, and the metals targeted, included:

- Effluent Treatment Plant in 1981: All metals
- Modernization of the zinc plant in 1981: Zinc, cadmium
- Boliden Norzink process in 1981: Mercury
- Electrolyte purge recycle in 1981: Zinc
- Halide Leach Plant in 1982: Zinc
- Copper Products Plant in 1989: Copper, arsenic
- Thallium Removal Plant in 1989: Thallium
- Elimination of the electrolyte purge discharge in 1990: Zinc
- Collection and treatment of surface water runoff in 1993: All metals
- Indirect heat exchange in the lead smelter in 1994: Mercury
- Effluent treatment plant (ETP) lagoon in 1994: All metals
- TMT addition for Hg precipitation in 1995: Mercury
- Treatment of copper matte granulation water in 1996: Cadmium
- Eliminating slag discharge to the Columbia River in 1996 1997: Zinc, copper, and lead
- Roof drains and perimeter drainage in 1997: All metals
- Start-up of the Kivcet smelter in 1997: All metals
- Elimination of Sewer #7 discharge in 1998: All metals

Opinion #1: A variety of factors likely contributed to Mr. Heinze's decision to locate his smelter at Trail:

- Proximity to Rossland ore
- Proximity to rail and river transport for raw materials and products
- Access to fuel, flux (slag additives), and reductant (coal, coke, wood)
- Access to a reliable skilled work force
- Proximity to the Kootenay River for hydroelectric power
- Proximity of clean creek water at suitable head
- A reasonably isolated location for release of smoke
- Proximity to the Columbia River for solid and liquid waste

Opinion #2: When comparing Figure 1 to Figure 2, it appears that the direction of slag discharge from the Trail smelter was likely down the bluff toward the Columbia River, rather than down the bluff toward the buildings.

Opinion #3: Based on examination of Figure 2, it appears that if slag had not already reached the Columbia River in 1896, it is likely that slag would have done so by the end of the century, four years later.

Opinion #4: Based on Figure 3, I conclude that slag discarded toward the Columbia River would have passed over the wall and entered the river prior to 1930. This slag must have been generated from both copper and lead smelting.

Opinion #5: Early copper slags at Trail were air-cooled, rather than granulated in water. These slags would likely therefore be found in larger chunks, i.e., substantially coarser than the relatively fine water-granulated slag. By 1907, the copper slag was being granulated.

Opinion #6: At Trail, when slag from copper smelting was granulated, similar granulation practice was also in place for slag produced from lead smelting.

Opinion #7: Relying on open burning – rather than furnaces equipped with means to collect a portion of the evolved dust and fume – resulted in a greater portion of the feedstocks' heavy metals exiting into the atmosphere. Therefore a lesser portion of the metals in Trail's feedstocks was available during this short period for disposal to the Columbia River.

Opinion #8: Installation of roasters equipped with means to collect a portion of the dust and condensed fume resulted in a greater portion of the metals in Trail's metallurgical feedstocks being available for disposal to the Columbia River.

Opinion #9: Acid production required thorough scrubbing of sinter-plant and roaster offgas. This scrubbing captured metal values that were now available for disposal to the Columbia River, rather than possible release to the atmosphere.

Opinion #10: Fine dust swept up the stack was likely enriched in arsenic (As) and cadmium (Cd). The basis for this conclusion is as follows:

- Arsenic and cadmium and their oxides and chlorides are easily volatilized.
- A significant portion of the As and Cd condenses on dust surfaces.
- Most of this surface is associated with the finer dust fractions.
- Fine dust settles slowly, and thus more readily passes through settling chambers into the stack, then to the atmosphere.

A portion of the As and Cd, as well as most of the mercury (Hg), does not condense. This uncondensed fraction is swept up the stack as fume.

Opinion #11: Relying on settling chambers to capture dust and condensed fume resulted in the release of substantial portions of arsenic and cadmium, and most of the mercury, in Trail's metallurgical feedstocks to the atmosphere. The greater the loss of these metals to the atmosphere from Trail's metallurgical dust settling chambers, the lower was the portion of these elements in Trail's feedstocks that could report directly to the Columbia River.

Opinion #12: Addition of hot Cottrell precipitators in 1914 decreased the quantity of arsenic and cadmium escaping into the atmosphere. This decrease resulted in a greater fraction of these metal inputs becoming available for discharge into the Columbia River.

Opinion #13: Trail's Cottrell precipitators collected dust from humidified gas. Unless sufficient moisture was injected to form a liquid phase, direct discharge of the collected dust to the Columbia River was unlikely.

Opinion #14: Recovered flue dust typically contains metals that have significant economic value. Trail would therefore have made substantial effort to economically recover, rather than discard, these values.

Opinion #15: Blast furnace slag containing at least 15% zinc had substantial commercial value – if an efficient slag fuming process could be implemented. Slags having lower zinc content did not contain sufficient metal values to pay for the cost of fuming, and to provide a margin for profit.

Opinion #16: When Trail fumed its lead BF slag, the slag's arsenic, cadmium, lead, and zinc content was substantially lowered. Mercury is so highly volatile that its concentration in both lead BF and fumed slag would be very low.

Opinion #17: Annual blast furnace and fumed-slag production tonnages provided by Teck (TECK 0715785) appear to be reasonable. This conclusion is based on using data from Trail's published technical articles to calculate ten yearly slag tonnages in the period from 1913 to 1990.

Opinion #18: From about 1920 until 1930, Trail stored substantial tonnages of its zinc-rich BF slag (15 to 20% Zn) from lead BF production in anticipation of developing a process to recover this zinc. It therefore appears that Teck may have overestimated the quantity of slag that CM&S discharged to the Columbia River from 1920 to 1930 (TECK 0715785).⁴

Opinion #19: Blast-furnace slag generated prior to about 1918 was relatively low in zinc content (7 to 12%), and therefore was discarded. Teck shows no slag going to the Columbia River prior to 1920 (TECK 0715785, as provided by Teck).

Opinion #20: It appears that granulated lead BF slag produced at Trail between about 1901 and about 1918 was discarded into the Columbia river.

Opinion #21: Production of sulfuric acid required efficient cleaning of the dust- and fume-laden furnace gases. This cleaning included efficient aqueous scrubbing of the gas, which collected as an aqueous slurry most of the remaining As, Cd, Pb, and Zn, plus a substantial portion of the Hg.

Opinion #22: The efficient gas scrubbing prior to the acid plants substantially decreased loss of arsenic, cadmium, lead, zinc, and mercury to the atmosphere. Efficient scrubbing of gas fed to the acid plants resulted in a greater portion of arsenic, cadmium, lead, zinc, and mercury in Trail's feedstocks being available for discharge to the Columbia River.

Opinion #23: The upper limit of the amount of zinc tankhouse electrolyte purge that could be consumed in Trail's fertilizer operation was the amount of zinc micronutrient that could be marketed. The amount of zinc that could be marketed as micronutrient was usually substantially less than the amount of zinc purged.

Opinion #24: Controlled removal of impure lead tankhouse electrolyte permitted processing of the electrolyte, prior to its disposal to the Columbia River, to recover a substantial portion of its lead and fluosilicic acid values. Thus, the greater the ratio of

⁴ But note that not all of the slag was stored during this period; see Figure 14.

controlled electrolyte removal to electrolyte loss, the less lead and acid reported to the river.

Opinion #25: Until baghouses were installed in 1951 to more efficiently recover dust and condensed fume from lead blast-furnace offgas, a greater portion of the cadmium and arsenic in Trail's feedstocks had been exhausted to atmosphere. To the extent that less cadmium and arsenic exhausted to atmosphere after baghouse installation on the lead BFs in 1951, more Cd and As were available for discharge to the Columbia River.

Opinion #26: To the extent that minor metals such as arsenic, cadmium, copper, and mercury were recovered as byproducts, less of these metals were available for discharge to the Columbia River.

IX. COPPER SMELTING AT TRAIL: 1896 to 1930

The descriptions below of CM&S copper processing practices introduce vocabulary essential for understanding Trail's subsequent lead and zinc smelting and refining metallurgy. Similar equipment was used in subsequent decades, albeit modified and improved. Copper ore and concentrate smelting at Trail ceased in 1930 due to a scarcity of feedstocks.

A. Definition of Copper Smelting; Slag Byproduct Utilization

Copper smelting is based upon the strong affinity of copper (Cu) for sulfur (S), and copper's weak affinity for oxygen (O) in comparison with iron (Fe) and other base metals. During smelting, a portion of the solids fed to the furnace vents as dust, fume, and gases. Most of the balance exits as matte, metallics, and slag.

A slag is not necessarily a waste. Slag may contain significant metal values: e.g., copper, zinc, iron, antimony, tin, indium, and/or germanium. A slag could therefore be economically processed immediately for additional values, ideally before solidification. Or the slag could be inventoried for such time as suitable equipment, and/or financing, becomes available. Slag can also be sold for use as aggregate, ballast (base for railroad tracks), cement-kiln or concrete additive, or for other applications.

Key is that the slag meets physical, chemical, and environmental specifications for the particular application.

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B. Copper Blast-Furnace Matte Smelting

Blast furnaces (see Figures 8 and 9) provided an important means for smelting Trail's copper feedstocks, and for processing lead concentrates. Thermal pretreatment (roasting/sintering) was often necessary to adjust feedstock sulfur content, and/or to agglomerate feedstock fines. These pretreatments will be described in a subsequent section of this report.

A blast furnace (BF) consists of two major parts, the *shaft* and *crucible*. The shaft is fed ore, coke, and flux from the top, where the venting gases are also withdrawn. As feedstocks descend down the shaft, hot gases rise up through the charge. Efficient BF operation thus requires that the feed be relatively coarse to permit gases to escape.



Figure 8. A water-jacketed blast furnace (Queneau, CSM class slide)

At the bottom of the shaft (the *bosh*, where the shaft funnels inward) are *tuyeres*. *Tuyeres* are pipes through which air is forced into the base of that shaft to provide oxygen. Oxygen supports combustion of the coke, and oxidizes a portion of the sulfide sulfur to sulfur dioxide.

The BF crucible extends downward from the tuyere level. This crucible holds the matte and slag; slag floats on top of the matte. The two phases are *tapped* (removed from the crucible) separately and at different levels through tap holes. In later years, these liquid outputs were collected in an external basin (*settler*), which improved gravity separation of the matte from the slag.

The principal slag additives (fluxes) at Trail were *limestone* (calcium carbonate), iron oxide, and silica. These additives were adjusted such that the BF slag had an appropriately low liquidus temperature. The fused BF slag was formulated to be sufficiently fluid to permit its separation by gravity from the much denser (but highly fluid) matte.



Figure 9. Blast furnace – a section view (Levy, 1912, p 138)

Gaseous products from BF smelting carried a considerable load of dust and fume. Typical dust load from the copper blast furnace was at least 2% of the charge; 5% was more typical, and even larger quantities were often produced. Dust was usually higher in copper content than the original charge due to the brittleness of the copper sulfide minerals. There was therefore substantial economic incentive to recover this dust.

Chambers of enormous capacity were required to provide the fine solid particles an opportunity to settle by decreasing velocity and cooling. Unsettled fines exhausted out of the stack. This means of offgas handling was standard practice not only at Trail, but worldwide.
Gaseous metal, i.e., fume, was carried with furnace exit gas. As the gas cooled, a large portion of the fume condensed. Metal-rich solids appeared both as difficult-to-collect extreme fines, and as coatings on dust particles. In fact, fume could be so difficult to collect that a baghouse was needed. The description below further describes fume behavior in a smelter (Levy, Univ. of Birmingham, 1912, p 168):

[Values] in the form of volatilized metallic products are also conveyed by the gases, particularly when lead, zinc, arsenic, etc., are present in the furnace charge, and these are carried forward in the form of fume. They tend to solidify as the temperature of the gases becomes lower, although their settling is very greatly impeded owing to the exceeding minuteness of their particles and also to their dilution; the problem of separating and collecting them is in consequence attended with great difficulty....

Where large quantities of lead, etc., are present some bag-house system of fume filtration is necessary, especially if silver be present, since this metal tends to be carried over in the leady fume. At the majority of copper smelters such extreme requirements are rarely necessary, although modern legislative requirements make severe demands on the managements for the freedom of the gases from injurious constituents.

The settled and collected BF dust could be smelted with roaster calcine in a RVF (reverberatory furnace), or returned to the BF if the dust was first briquetted. Trail had briquetting machines. The role of *baghouses* and electrostatic precipitators (Cottrells) for offgas treatment will be discussed in a subsequent section of this report. A Cottrell and an electrostatic precipitator are the same thing.

No Cottrell was used to collect dust from gases evolved from the copper blast furnace. Dust was collected in balloon flues by settling.

C. Copper Reverberatory Matte Smelting

Although the blast furnace was the most economic means to smelt lumps and coarse particles of copper-bearing ores, this furnace was not acceptable for fines. Blow-out of fine dusty ore from the BF could be as high as 10%. Briquetting fine feed, along with the recycled dust, was a significant cost. Fine ores and concentrates were often therefore more economically processed in reverberatory furnaces (RVFs).

A RVF was (and still is) an elongated brick structure enclosing an essentially horizontal space with a *hearth* (floor) upon which ore or concentrate was placed. See Figure 10. The charge would have best been free from lumps,

finely divided, and roasted (detailed later) so that sulfur content would be limited to that needed to generate the matte.



Figure 10. Tapping a reverberatory furnace (Queneau, CSM class slide)

A fire box heated the RVF from one end using highly bituminous coal (resinous wood was sometimes also added) to produce a long flame. Doors on the side of the furnace provided access to skim off reverberatory furnace slag. Matte product was tapped from the back end of the hearth close to hearth level. Smoke vented into the flue leading to the smokestack. The smoke consisted of dust, fume (vaporized metals), and gas (nitrogen, steam, carbon monoxide and dioxide, excess oxygen, etc.). Larger dust particles settled from the smoke prior to exiting the stack.

D. Roasting or Sintering of BF and RVF Feedstocks

The objective of roasting sulfide copper ore prior to smelting was to oxidize a portion of the sulfur and iron, and to remove volatile impurities such as arsenic (As), antimony (Sb), and bismuth (Bi). Sixty to 97% of the arsenic and 20 to 85% of the antimony were volatilized from copper sulfide ore via roasting (Hofman, 1914, p 65). The roasted ore could then be efficiently smelted to matte having high copper concentration and relatively low As, Sb, and Bi impurity.

The Herreshoff roaster shown in Figure 11 was a brick-lined vertical cylinder. An air-cooled central shaft supported arms that raked six hearths. Solids descended from hearth to hearth. At Trail the Herreshoffs were mounted above the RVF, thus providing direct feeding to hot calcine (Carlyle, 1896, p 18). Calcine discharged from the roasters needed to be *sintered* (agglomerated) prior to smelting in the blast furnace. Circular pot calciners served this purpose – and also removed additional sulfur.

The quantity of ore roasted per unit of hearth area increased dramatically between 1896 and 1916. Heap roasting at the turn of the century processed 5 to 20 lb ore/ft² of hearth per day. By 1925, D&L sintering achieved 2000 to 3000 lb ore/ft² of hearth per day (Liddell, Vol 1, 1926, p 303).



Figure 11. Herreshoff multiple-hearth roaster (Levy, 1912, p 74)

Dwight & Lloyd (*D&L*) continuous sintering displaced both roasting and earlier methods of thermal agglomeration. The first D&L unit was brought on line in 1910. Trail had installed a D&L machine for its copper concentrates (1% Cu and 1 oz Au/ton) by 1913 (Hayward, 1924, p 107). A 1950s model of this key piece of equipment at Trail, in this case for sintering lead concentrates, is shown in Figure 12. D&L sintering is a continuous rather than a batch process. This machine produces better sinter, consumes less labor, requires less floor space, and thus incurs a substantially lower operating cost.



Figure 12. Dwight & Lloyd (*D&L*) continuous sintering machine (Anonymous, 1954, p 239)

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Agglomerated fluxed ore and coke mixture was placed on pallets (grates) that had been pre-coated with limestone to minimize sticking. The sulfide fraction was then ignited. As the ignited mixture passed over the suction box, air was drawn through the mix to complete sintering and to oxidize most of the sulfide sulfur. The sinter then cooled, and was discharged from the pallets. The grates continued in the loop to accept fresh feedstock.

E. Slag Output from Copper Matte Smelting

The primary fused outputs from copper matte smelting were matte and slag. Copper slag at Trail was "granulated and carried away by streams of water very conveniently and cheaply" (Turnbull, <u>Canadian Mining Journal</u>, 1907, p 424). Hofman (1914, pp 174) describes waste copper slag being granulated by a jet of water followed by disposal in a dump or into a river at the Mond Nickel Works in Ontario. Austin describes the slag granulation process at an unspecified location as follows (1909, pp 325-326):

A cast-iron launder is arranged to receive the slag as it falls from the spout of the forehearth. The launder has a grade of 1 inch to the foot, and through it water is made to flow constantly. In addition, a horizontal flattened jet of water strikes the falling slag, instantly cooling and breaking it into granules of various sizes averaging one-sixteenth of an inch diameter. The flow of water carries the slag to the dump.

The quantity of slag generated during matte smelting depended on the factors listed below.

- <u>Ore gangue content</u>: The quantity of SiO₂, Fe(Mn)O, Ca(Mg)O, Al₂O₃, and ZnO in the ore. Silicon, iron, calcium and aluminum are more comfortable as oxides rather than metals.
- <u>Flux addition</u>: The quantity of flux that must be added to the furnace to produce a suitable slag. Trail smelter operations eventually were able to blend diverse feedstocks such that need for flux became minimal, i.e., essentially just limestone was used.
- <u>Copper content of ore and matte</u>: The grade (copper content) of the matte, and the copper content of the feed. The lower the Cu:Fe ratio in the matte, and the higher the copper content of the furnace feed, the greater the portion of feed iron that reported to the slag.
- <u>Fuel ash content</u>: The ash content of coke and other fuels that ended up in the smelting portion of the furnace transferred to the slag. The BF coke typically contained at least 10 to 12% ash, most of which reported to the

slag. Early reverberatory furnaces burned coal in a firebox, thus permitting separate recovery of the ash.

F. On-Site Conversion of Copper Matte to Refined Copper

For copper at Trail, 1916 was a key date. The plant installed the converting and refining capacity to produce electrorefined copper from its matte. The metallurgical steps for this plant upgrade are summarized below (Young, <u>Eng.</u> <u>& Mining Journal</u>, 1923, pp 141-44; Anonymous, 1925, p A 258).

- <u>Converting matte to blister copper</u>: Matte was blown with air in two Great Falls converters to blister copper (about 95% Cu), impurity-rich slag, and dusty SO₂ offgas. See Figure 13. Siliceous ores, plant scrap / cleanups, and recycled converter flue dust were converted along with the matte. Copper-rich converter slag returned to the three blast furnaces used to produce the matte.
- <u>Gas cleaning</u>: Electrostatic precipitators (Cottrells) collected the converter dust. In a Cottrell, the air carrying the dust was ionized. Air conductivity was enhanced by its SO₂ content. Dust particles in this media gathered sufficient electric charge to move under the force of the electric field, and to thus be collected.
- <u>Production of electrorefined copper</u>: The blister copper was further purified and its oxygen content adjusted (in a separate furnace) to produce flat anodes. The anodes were then electrolytically refined to produce highpurity copper cathodes.

Copper tankhouses used electricity to dissolve copper from the impure anode, then selectively plated the copper to produce a pure cathode. Gold and silver were recovered from the anode slimes. Copper tankhouse technology has many similarities to that used for Betts electrolytic lead refining (to be described later in this report); refer back to Figure 4.

Trail purged arsenic (As) and antimony (Sb) from the copper refinery by returning black copper containing the rejected As and Sb to the copper blast furnace, where arsenic and antimony were eliminated by venting up the stack (Young, 1923, p 144).



Figure 13. Early copper converters at use in the Trail smelter (Fish, 1997, p 92)

G. Opinions from Section IX

Opinion #27: Slag is not necessarily a waste. Economic value can include the slag's contained metals, or its use as aggregate, ballast (base for railroad tracks), cement-kiln additive, and/or concrete additive.

Opinion #28: Trail slag from copper operations contained substantial concentrations of silica, iron oxide, and calcium oxide, as well as small quantities of copper matte.

Opinion #29: Smelter flue dust at Trail typically contained sufficient metal values to provide economic incentive for its recovery.

Opinion #30: Relying on settling to collect furnace dust and fume – rather than its collection by Cottrells, baghouses, and/or scrubbing – resulted in a greater portion of feedstock heavy metals exiting via the stacks. Therefore, prior to more efficient dust and fume collection at Trail, a lesser portion of metallurgical feedstock heavy metals was available to report to the Columbia River.

Opinion #31: Granulated copper slag produced in the early 1900s appeared to be about one-sixteenth of an inch diameter. My more recent experience with granulated slags is that little has changed: the bulk of the slag's weight is on the order of one-sixteenth of an inch diameter.

Opinion #32: Most of the arsenic in the feedstocks fed to Trail's copper smelter between 1896 (initiation of copper smelting) and 1930 (cessation of copper smelting) was vented to atmosphere.

X. LEAD OPERATIONS AT TRAIL – THE EARLY YEARS: About 1900 to 1929

When lead production at Trail began between 1899 and 1901, its metallurgical practice was standard for the time. Ore was roasted in ten hand-rabbled RVFs and six Bruckner furnaces, followed by reduction in three blast furnaces. The Bruckner was a rotary furnace, i.e., a horizontal rotating brick-lined cylinder fired along its central axis. Blast-furnace bullion output, with its substantial silver values, was shipped to San Francisco for refining.

A. Specifics on the Early Years of Lead Operations

- Lead ores came to Trail mainly from the East Kootenay, Slocan and Lardeau (B.C.) districts. Ore suppliers included the St. Eugene Mine and the Snowshoe Mine at Phoenix, B.C. The former provided 75% of the smelter's lead output. Trail also purchased additional lead bullion and mill products from other smelters.
- Prior to ramping up of the Sullivan mine (1915), diversity in ore gangue content minimized need for flux. Efficient ore smelting was attained using limestone, plus minor quantities of iron oxide and silica for trim.
- After initiating Betts electrolytic lead refining in 1902, Trail marketed its lead output directly. Precious metals, which concentrated in the tankhouse slimes, were sold separately. Trail lead-production capacity increased from 10 stpd (1902) to 20 stpd (1904) to 50 stpd (1905) to 75 stpd (1906). The silver refinery was started up in 1908, as was a plant to manufacture fluosilicic acid for the Betts electrolyte (from calcium fluoride and silica).
- By 1908, eight Huntington & Heberlein (H&H) circular roasters and 24 H&H pot calciners replaced ten hand-rabbled roasting furnaces. Two briquetting presses, each equipped with a pug mill, agglomerated the fines. Roasting was carried out in Wedge multiple-hearth furnaces.
- Ample water from three creeks flowed to the smelter at 100-ft head via five miles of wood pipe. Good quality high-ash coke and coal arrived from Fernie and Michel, B.C., about 240 miles east of Trail. Up to 200 stpd of limestone flux (50% CaO) was shipped in from Fife, B.C. Target lead BF slag

composition was 31 to 33% SiO₂, 24 to 30% Fe(Mn)O, 18 to 20% Ca(Mg)O, 8 to 16% Al₂O₃, 7 to 12% Zn, and 1% Pb (McNab, 1909a, p 431). This BF slag was discarded.

- By 1917, Trail was using two stages of Dwight-Lloyd sintering to prepare its BF feed. This upgrade eliminated the need for Wedge roasters and pot calciners. The blast furnace slag assayed 32% SiO₂, 29% Fe(Mn)O, 20.5% Ca(Mg)O, 6.5% Al₂O₃, 10% Zn, and 1.5% Pb (Hofman, 1918, p 221). The BF slag was still relatively low in zinc content (10%). It was only when the majority of the lead-zinc feedstock came from the Sullivan mine (shortly before 1920) that the zinc content of lead BF slag became sufficiently high to be of economic interest.
- An average lead BF slag analysis in 1922 was 15.8% SiO₂, 33% Fe, 6% CaO, 17 to 21% Zn, and 2.4% Pb (Buchanan, 1922, pp 532-533). Young in 1923 (p 141) provided the following BF slag composition: 18% SiO₂, 31% Fe, 9% CaO, 3% Al₂O₃, 18% Zn, and 1.7% Pb. Note the relatively high zinc and iron content, and the relatively low silica and lime content, as compared to the BF slags generated in 1917.
- By 1925, most of Trail's lead feed was Sullivan concentrate having a typical assay of 66% Pb, 6.3% Zn, 18.8% S, 7.5% Fe, and 1% silica (Anonymous, B.C. Minister of Mines, 1925, p A254). Also fed to the lead blast furnace was zinc leach plant residue, e.g., 10.9% Pb, 19.1% Zn, 3.5% S, 37% Fe, and 1% silica. See Figure 14 for the overall flow diagram of the lead smelter.

Comments to provide an understanding of Figure 14 are as follows:

- Recycling zinc plant residues to the lead BF required that BF feed be iron-rich and sulfur-poor. Smooth BF operation could then be maintained, outputting BF slag assaying 16 to 17% Zn. Before the introduction of slag fuming at Trail, the slag was granulated and stored awaiting the development of a process for the recovery of its zinc and lead (Murray, Cominco, 1936, p 67).
- Figure 14, which was published in 1925, shows lead BF slag going to "Waste". The associated text in this paper reads: *The slag is granulated and conveyed to the slag-dump by launder*. This BF slag reportedly assayed 16 to 17% Zn.



Figure 14. Lead smelter flow (Anonymous, B.C. Minister of Mines, 1925, pp A255)

- There nevertheless is ample evidence that substantial quantities of high-zinc slag were inventoried by CM&S for later economic recovery of contained metal values, e.g., ...some 500,000 tons of old slag, running about 20% Zn, has been accumulated (Mason / Cominco, 1929, p 342).
- Research at Trail initiated in 1920 ultimately developed an economical process (slag fuming, commercial by 1930) for recovering contained values from BF slag. During the interim, BF slag was relegated to large stockpiles (Yurko, 1970, p 331). Beginning in 1930, lead BF slag was withdrawn from

inventory and fumed, along with current production, to recover residual lead and zinc values.

- Cottrells were first installed in 1914-15 to process dust- and fume-laden gases from blast roasting, smelting, and converting. The Cottrell-treated gas vented into two balloon flues, thence into a single flue leading to the stack. By 1933, eleven Cottrells had been erected for dust removal from various gases (Hofman, 1918, pp 457-458; Murray / CM&S, 1933, p 81).
- A problem was the disparity between the output of zinc plant residue and the capacity of the lead smelter to treat it. Over the years the residue stockpile grew.
- Offgas, fume, and dust from sintering and BF operations passed through Cottrells prior to discharge to the balloon flues. The dust was briquetted, then returned to the BF via the sintering machines.
- Copper matte byproduct produced from drossing the BF bullion went to the copper converters (refer back to Figure 13).
- The drossed lead bullion was cast into Betts anodes. These anodes were then hung in tanks alternately with thin cathode starting sheets of refined lead for electrorefining; refer back to Figure 4. After eight days in a fluosilicic acid electrolyte, most of the lead in the anodes had transferred to the cathode starting sheets. Precious metals and impurities in the anodes remained as a black slime in the tanks, for subsequent recovery.

B. Opinions from Section X

Opinion #33: Efficiently blending feedstocks purchased from a wide variety of sources not only minimized flux consumption, but also substantially decreased the quantity of waste slag generated per ton of metal produced.

XI. ZINC OPERATIONS AT TRAIL – THE EARLY YEARS: 1916 to 1929

In 1912, Trail began researching methods to recover zinc by electrolyzing purified zinc sulfate solution. Meanwhile, selective mining and hand sorting of zinc-rich mineralization at the Sullivan mine produced concentrates assaying 25 to 35% Zn. By 1916, production of electrolytic zinc had begun.

Trail's electrolytic zinc plant was profitable, due principally to the high zinc prices associated with metal needs during World War I. Lead exited the process (along with residual zinc) as insoluble sulfate – a suitable feed for the lead BF.

A. Specifics on the Early Years of Zinc Operations

- Sullivan zinc concentrates were dried, then passed through six multiplehearth Wedge roasters to reject sulfur as SO₂. Roaster output was primarily ZnO calcine. Offgas passed through Cottrells to a 200-ft stack. Acid plants built in 1916-17 provided the sulfuric acid needed for *leaching* the roaster calcine (TECK 0279510).
- Leaching involves mixing calcine with sulfuric acid to dissolve zinc oxide, generating zinc sulfate (ZnSO₄) electrolyte. Impurities, including copper and cadmium, are subsequently precipitated from this electrolyte by addition of zinc dust. The purified zinc-rich electrolyte (on the order of 150 gpl Zn) goes to a tankhouse for electrowinning (EW) of zinc cathodes. I am using the present tense, because this process continues at Trail to this day (September 2010).
- As zinc sulfate reduces to zinc metal in the tankhouse, the associated sulfate ion remains behind as sulfuric acid. This sulfuric acid (including on the order of 50 gpl zinc) is returned to leaching to dissolve additional zinc. However, a portion of this electrolyte must be purged to control impurities.
- The purged portion of the zinc tankhouse electrolyte was *stripped* and discarded daily to control both the volume and purity of the retained electrolyte. Stripping the 50-gpl zinc-electrolyte purge involved a second electrolysis process that reduced its zinc content to 15 gpl to 18 gpl. This striped solution was discarded to the Columbia River.
- The residue produced by leaching zinc concentrates contained most of the lead fed to the zinc roasters. A substantial portion of this leady residue, along with unleached zinc ferrite, was therefore returned to the lead blast furnaces. Often the BFs had insufficient capacity for this residue; the excess was inventoried until additional BF capacity became available.
- Sullivan mine zinc output continued to increase, resulting in increased output and inventory of zinc-rich BF slags. An economic means was therefore needed to recover rather than to lose this zinc and associated lead in the discard BF slag – a worthy target for corporate research. An important secondary benefit of developing a BF-slag treatment process would be

removing a key BF operating constraint: the need to target production of BF slag assaying <2% Pb.

- Trail's roast-leach-EW process for zinc provided important opportunities to recover minor metals, e.g., cadmium, the recovery of which began in 1927 (TECK 0279511). These minor-metal recovery processes minimized loss of metals to the environment.
- Zinc concentrate roasting also provided means to economically recover sulfuric acid. Acid recovery opened the door to economic production of fertilizer. Fertilizer production led to economic production of major quantities of tonnage oxygen to improve efficiencies in Trail's lead, zinc and acid production operations.

B. Opinions from Section XI

Opinion #34: When Trail implemented a wet process in 1916 to recover zinc, i.e., leaching and electrowinning, aqueous zinc and associated impurities were at that time available for discharge into the Columbia River.

Opinion #35: Substantial quantities of stripped spent zinc electrolyte (15 to 18 gpl Zn) were purged for discharge into the Columbia River or Stoney Creek from 1916 to 1990.

XII. LEAD, ZINC & FERTILIZER – THE MIDDLE YEARS: 1930 to 1979

By the *Middle Years* is meant the half century beginning in about 1930, when slag fuming, flash roasting, and fertilizer production began. (A major modernization began in 1979, culminating with conversion to Kivcet smelting in 1997.) Events of particular significance during these middle years include the following:

A. Fuming of Blast Furnace Slag

In 1930, injecting molten BF slag with air and coal began. This fuming process volatilized, oxidized, then collected condensed lead, zinc, and minormetal values from the BF slag in a baghouse. A baghouse captures dust by passing the gas through supported cloth socks. The dust is periodically released from the socks either by shaking, or with a puff of air. Slag fuming volatilized about 85% of the zinc, plus nearly all of the lead. Addition of excess air oxidized the Zn^o- and PbS-rich fume to ZnO and PbO / PbSO₄, which were collected as dust. Lead in the BF slag was thus reduced from <3% to $\approx 0.1\%^5$; zinc content was reduced from $\approx 18\%$ to $\approx 2.6\%$. Non-volatile metals remained in the fumed slag, e.g., copper assayed about 0.5%.

A variety of minor metals also fume from the slag. For example, cadmium (Cd), arsenic (As), tin, indium, germanium, and silver compounds have appreciable vapor pressure at Pb-Zn fuming temperatures. These impurities are thus mostly driven into the ZnO-rich fume product. Cadmium content of BF slag was decreased from $\approx 0.01\%$ to $\approx 0.001\%$; arsenic content was reduced from $\approx 0.15\%$ to $\approx 0.01\%$ (TECK 0099157).

In 1931, Trail's fuming furnace processed 150,000 tons of BF slag. The fumed slag output went to waste. Figures 15 and 16 illustrate Trail's slag fuming practice.



Figure 15. Charging a BF slag fuming furnace at Trail (Yurko / Cominco, 1970, p 340)

⁵ The " \approx " symbol in front of a number shows that the number is an approximate value. PBQ – Expert Opinion - 9/15/10



Figure 16. Trail's water-jacketed fuming furnace with 35 tuyeres (McNaughton / CM&S, 1936, p 723)

 It was no longer necessary to produce BF-slag having low lead content. Five percent lead (rather than targeting <2%) in BF slag was now acceptable, because the fuming furnace volatilized almost all of the remaining lead. The BF therefore became much easier to operate; both coke consumption and flux cost decreased.

Possibly the most notable feature in connection with the slag-fuming plant at Trail is the effect it has had on blast-furnace smelting practice for lead. It...marks the most important development in Trail lead-metallurgy since the introduction of sintering (Murray / CM&S, 1933, p 100).

- The ZnO-rich fume was leached with acidic sulfate solution to recover zinc and minor metals. The lead-sulfate-rich leach residue recycled back to the sintering and the BF.
- A problem was the disparity between the output of zinc plant residue and the capacity of the lead smelter to treat it. By the end of World War II, the pile had reached *the formidable total of half a million tons* (Mitchell / Cominco, 1957, pp 361). Residue processing capacity was substantially expanded in 1955-56 when sinter-plant equipment was upgraded, including wet-mix drying (360 F exhaust temperature) of the feed.
- In addition to BF slag and flue dust, the fuming furnace processed zinc dross, cadmium residues, furnace and ladle skulls, and miscellaneous plant reverts.

B. Suspension Roasting of Zinc Concentrates

By the late 1920s, the need to capture rather than vent SO_2 emissions became a major priority. In 1928, some 9,600 tons of sulfur per month were discharged to atmosphere in the form of sulfur dioxide gas (Anonymous, Canadian Mining Journal, 1954, p 308). Young (1931c, p 416) describes the technical barrier to economic capture of the sulfur dioxide, i.e., SO_2 concentration in the gas too dilute to be economically captured.

Young then alludes to what later became the basis for an economic solution: implementation of flash roasting to generate strong (6 to 8%) SO₂. An additional benefit of the new process is additional capture of Cd, Bi and Sb. Young's description is as follows:

Gases from the lead blast furnaces and the sintering furnaces are so dilute that it is impracticable to do more than is being done with them – to remove fume and dust suspensions. On the other hand, the gases from zinc roasting contain higher and more controllable amounts of sulphur dioxide. Roasting practice is being studied, and a new method of roasting is being experimented with. The objective is....a gaseous product containing about eight per cent of sulphur dioxide. This product will be handled in sulphuric acid plants now under construction. In addition to the utilization of this gas, other byproducts are produced – cadmium, bismuth, and antimony.

The new method that soon led to economic sulfuric acid production was *suspension roasting*. By 1936 the Wedge multiple-hearth roasters had been converted over to this new technology. See Figure 17. Removing the middle hearths of the roasters extended the time that the ignited sulfide particles spent in free fall. Capacity was tripled. A decade later others would develop similar technology for *flash roasting* copper and nickel sulfides.

 Conversion to suspension roasting not only increased roaster capacity, but also improved process control, eliminated secondary roasting for final sulfur removal, attained higher zinc solubility, permitted more efficient dust collection, attained additional heat recovery, and generated higher SO₂ concentration. The increased SO₂ concentration substantially improved the economics of acid production. This increased concentration soon made it economic to convert over 90% of the plant's sulfur input to sulfuric acid.



Figure 17. A suspension multiple-hearth roaster with boiler (26), cyclone dust collector (27), balloon flue (29), Cottrell (30), and acid plant (31), from Stimmel, 1936, pp 542

Gas exiting the roaster carried about 40% of the furnace charge. About 20% of this dust settled in the waste heat boiler; this 20% of the dust was sent to zinc leaching. Cyclone separators recovered 90 to 95% of the remaining dust for additional roasting. About 95% of what dust remained was then collected by Cottrell electrostatic precipitation; this latter dust also went to leaching. The SO₂-laden gas, containing on the order of 0.2% of roaster feed, then continued on for extensive additional cleaning prior to conversion to sulfuric acid.

Highly volatile minor metals, e.g., Cd, As, and Hg, reported to roaster offgas. A significant portion of these metals reported to the 0.2% of the roaster dust that passed through the Cottrells.

Because catalysts used in manufacturing sulfuric acid are easily damaged (poisoned), the acid-plant feed must be thoroughly cleaned to remove as much of these metals (and other contaminants) as possible (Davenport,

Univ. of Arizona, 2006, pp 31-45). This gas scrubbing generates slurry discharge that provides opportunities for additional minor-metal recovery.

C. Sulfuric Acid Output Leads to Fertilizer Production

In 1931, CM&S expanded its Trail operations to include manufacturing of ammonium sulfate and ammonium phosphate fertilizer. Warfield Flat is a high terrace overlooking Trail's metallurgical plant. It was here in 1930 that CM&S initiated construction of a 65-acre fertilizer production facility to utilize byproduct acid and energy output from the smelter. Steam generated from waste-heat boilers at the slag fuming plant was transferred in a well-insulated 12-inch pipe about a mile to Warfield Flats. This steam concentrated fertilizer solutions derived from the smelter's sulfuric acid output.

Markets within reasonable shipping distance from Trail initially could not absorb all the sulfuric acid potentially available (King, 1950, p 2243). It took until 1944 for fertilizer markets to consume this substantial acid output (Kirkpatrick, 1949, p 972). Figure 18 is a simplified representation of the relationship between the zinc plant and the fertilizer plant. This figure appears to depict Trail after 1980 (when pressure leaching of zinc concentrates began), but before 1981 (start-up of the effluent treatment plant).

Operations at Warfield Flat included manufacturing sulfuric acid, pure sulfur dioxide, oxygen, nitrogen, hydrogen, ammonia, phosphoric acid, ammonium phosphate, ammonium sulfate, nitric acid, ammonium nitrate, and hydrofluosilicic acid. Aqueous effluents from the fertilizer plant included mercury and zinc.

Acidification of phosphate rock produced not only phosphoric acid, but also gypsum (hydrated calcium sulfate) precipitate and silicon tetrafluoride gas. The phosphoric acid was reacted with ammonia to produce ammonium phosphate fertilizer. A small quantity of the gypsum was sold into agriculture. The balance went to waste.



ZINC OPERATIONS: MOST COMPONENTS ARE MODERN TECHNOLOGY

Figure 18. A simplified Trail zinc-processing diagram, including fertilizer operations (TECK 0099142; ca. 1980)

Water scrubbing of the fluoride-rich byproduct gas (evolved when manufacturing phosphoric acid) produced hydrofluosilicic acid. This acid served as electrolyte make-up in the lead refinery. Kirkpatrick states in 1949 that several tons of this acid were consumed daily (p 975):

[Lead refining requires] several tons each day of hydro-fluosilicic acid to maintain the proper acid balance in the cells. Until a few years ago all or part of the hydro-fluosilicic acid required for the refinery was made from fluorspar, sulfuric acid, and silica. Now... there is an adequate supply of hydro-fluosilicic acid as a chemical plant byproduct.

D. Fertilizer Production Leads to Smelter Process Efficiencies

To produce ammonia, a key raw material for producing sulfate- and phosphate-based fertilizers, one inputs tonnage nitrogen and hydrogen. Trail produced its nitrogen by liquefaction and low-temperature fractionation of air; the byproduct was tonnage oxygen. The plant produced its hydrogen by electrolysis of water via its inexpensive hydroelectric power. The byproduct was additional tonnage oxygen.

Trail used oxygen produced in its fertilizer operation to improve smelter process efficiencies:

- Air fed to the BFs was enriched with oxygen. Furnace output improved, coke consumption decreased, and the furnace ran more smoothly. Offgas volume also decreased, enhancing offgas treatment capacity and/or efficiency.
- Trail also used oxygen to enrich the air fed to the suspension roasters. The result was improved roaster operation, throughput, and heat recovery. Use of oxygen also improved the efficiency and capacity of its sulfuric acid plants by generating higher SO₂ concentration in the roaster offgas. Roaster offgas went to acid plants.
- A further use of oxygen at Trail was to improve slag fuming. Oxygen enrichment improved both furnace output and zinc recovery, resulting in lower zinc content in the discard fumed slag.
- Ammonia produced in Trail's fertilizer plant was also useful in the sinter plant. Sinter-plant offgas (in the lead smelter) contained only 0.5 to 1% SO₂. The contact sulfuric acid plants needed at least 5% SO₂ for satisfactory SO₂ recovery and economics. To bypass this limitation, the sinter-plant Cottrell offgas was scrubbed with aqueous ammonia. Scrubbing captured the SO₂, producing ammonium bisulfite.
- Adding sulfuric acid and oxygen to the ammonium bisulfite solution liberated concentrated SO₂. This SO₂ was used both to enrich acid-plant feed gas, and for production of elemental sulfur. The product was ammonium sulfate feedstock for the evaporators at Warfield Flats. Ammonia was also used to scrub acid-plant tail (exhaust) gas to facilitate meeting SO₂ smelter environmental discharge standards.

Figure 19 provides a simplified diagram of Trail lead operations as they existed in the early 1930s. Note the absorption of sinter-plant SO_2 (in aqueous ammonia), and the fuming of BF slag.



Figure 19. Lead processing at Trail sometime after 1930 (TECK 0099142)

E. Recovering Dust and Fume from Furnace Offgas

In 1931, hot Cottrells were in use to clean offgas from Trail's sinter machines, blast furnaces, zinc roasters, and for the silver refinery (arsenic and antimony fume). Cottrells also rejected dust, fume, and mist prior to production of sulfuric acid. Weight of dust captured was substantial (Young, 1931d, pp 507-508):

- Sintering furnace circuit: 15 to 20 tons/day
- Blast furnace circuit: About 40 tons/day
- Zinc roasters: About 60 tons/day
- Silver refinery: 2 to 3 tons/day
- Acid-plant Cottrells: 1 to 1.5 tons of dust/day

Hargrave provided the following tabulation of dust and fume collection equipment in use at Trail in 1959 (p 367):

- Lead sinter-plant driers: 3 Doyle wet scrubbers
- Lead sintering: 5 Cottrells
- Blast furnaces: 20 baghouses
- Slag fuming: 16 baghouses
- Zinc roasting: 15 cyclones and 4 Cottrells

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- Silver refineries: 4 baghouses
- Antimonial lead plant: 2 baghouses

Where particularly efficient gas scrubbing was required, Trail relied on its Doyle wet scrubbers. When processing vent gases from wet-mix drying prior to lead sintering (1953), these units collected 98% of the dust. The Doyle scrubbers also processed large volumes of air ventilating the conveyers at the discharge of the sinter machines.

In 1962, Trail began adding halide (lead chloride) to its sinter-plant feed, probably to accelerate the fuming off of impurities, e.g., arsenic, cadmium, and thallium (Cominco, 1962, TECK 0279518).

Cottrell treatment of humidified BF flue gas attained over 95% dust collection efficiency. When the BFs were equipped with baghouses in 1951, dust collection efficiency exceeded 99%.

The major part of the sulfuric acid produced at Trail was made from zinc roaster offgas. To protect the acid-plant catalyst, this gas had to be thoroughly cleaned as follows (Cobleigh, 1932, pp 719-20):

- Cyclones first removed coarse dust.
- Most of the remaining dust was then collected in hot Cottrells.
- Scrubbing with dilute sulfuric acid followed.
- Next came water washing, followed by mist removal in a Cottrell.
- Final cleaning entailed gas drying in 80 to 93% sulfuric acid, followed by removal of entrained acid in a box filter filled with coke.

F. Minimizing Loss of Electrolyte in the Betts Process

The Betts process for lead electrolytically refines (rejects most impurities from) lead. It is similar to electrolytic refining of copper. Betts electrolyte in 1938 contained 67 gpl lead and 142 gpl total hydrofluosilicic acid; free silicic acid was 95 gpl (Huttl, 1938a, p 38). Gelatinous organic addition agents (*glue*) facilitated production of solid competent cathodes.

Of particular concern at Trail was decomposition of glue additive to amino acetic acids, which had no outlet from the system. High mechanical losses of lead electrolyte in the early years at Trail provided the purge from the Betts tankhouse. The Betts electroyte in 1924 contained 11 to 13% total H_2SiF_6 and 6 to 9% Pb. Electrolyte loss was 4 to 5 lb of H_2SiF_6 per short ton of pig lead

(CM&S Staff, 1924, p 457). In later years, dilution of the electrolyte that accompanied plant expansion offset losses. By the mid-1930s it became necessary to withdraw electrolyte from the system.

Lead was recovered from Betts electrolyte purge by addition of sulfuric acid to precipitate lead sulfate. About 75% of the residual acid was then recovered from the lead-stripped liquor. Work was initiated to substitute *Goulac* for a portion of the glue to minimize need for this electrolyte purge (Fingland / CM&S,1930, pp 184 and 190; pp 198-199; McIntyre, 1936, pp 280-81).

G. Cadmium Recovery

Cadmium recovery at Trail began in 1927. Most of the cadmium fed to Trail arrived in the zinc concentrate. During roasting, cadmium split between calcine, dust and fume. The roaster calcine and a portion of the flue dust were leached to generate electrolyte for zinc electrowinning. Dissolved cadmium was then cemented as *sponge* on zinc dust to generate the primary feed to the cadmium plant.

In the cadmium plant, the sponge was leached with sulfuric acid. Electrowinning the purified Cd-rich solution produced cadmium cathodes, which were melted, then cast into balls or slab (Anonymous, 1954, pp 280-81).

The calcine leach residue contained not only residual cadmium, but also zinc and lead. This residue returned to the lead smelter, where cadmium concentrated in the blast furnace dust. Prior to installation of BF baghouses (1951), cadmium was allowed to build up in the BF dust, which was periodically purged to the zinc roaster. Build-up was limited to 3.5% Cd to avoid excessive loss of cadmium to the atmosphere:

Experience had shown that if the cadmium content was allowed to exceed 3.5%, loss of cadmium through the treaters (Cottrells) *to the stacks became excessive* (Bainbridge, 1952, p 1306).

After the BF baghouses were installed in 1951, the Cd-rich BF dust was sent to the fuming furnace for concentration prior to leaching. Cadmium and its compounds are sufficiently volatile that slag fuming efficiently rejects this impurity.

H. Arsenic Recovery

Significant quantities of arsenic arrive at Trail in both the lead and zinc concentrates. Trail consumed a portion of it as an alloying element in lead, and as a raw material to produce copper arsenate for wood treatment. Arsenic is a particularly difficult impurity to work with because:

- Arsenic is toxic.
- The market for arsenic and its compounds is insufficient to economically consume Trail's output.
- Arsenic oxide volatilizes easily, but is not so easily that a clean separations is made between gas and solids.
- A substantial portion of the arsenic follows lead into the lead refinery, and ultimately into the silver refinery.

The result is that much of Trail's arsenic input ultimately accumulated on site as arsenic-rich flue dust in stockpiles. In the early years, much of the arsenic exited via the stacks. By the 1930s, dust collection became more efficient. Furthermore, excellent cleaning of fume-laden offgas was necessary prior to its use to produce sulfuric acid.

Arsenic and its compounds are sufficiently volatile that slag fuming efficiently rejects this impurity.

I. Opinions from Section XII

Opinion #36: By producing ammonia- and phosphate-based fertilizers, Trail provided tonnage oxygen, ammonia, and hydrofluosilicic acid to its metallurgical operations. The result was being able to economically 1) scrub dilute sinter-plant offgas, 2) improve the efficiency of its furnace operations, 3) lower the zinc content of its fumed slag, 4) increase the capacity of its furnace-offgas processing plants, and 5) have the ammonia needed to precipitate zinc from its zinc tankhouse purge electrolyte.

Opinion #37: Wet scrubbing of cadmium-rich vent gases from wet-mix drying prior to lead sintering increased the potential for cadmium to be discharged to the Columbia River, as did scrubbing of air ventilating the conveyers at the discharge of the sinter machines.

Opinion #38: Electrolyte containing a high concentration of soluble lead was lost or purged from Trail's lead refinery prior to 1930. As a result, about 2 lb of lead per ton of

Pb cathode output (4.5X67/142) was likely flushed into the Columbia River between 1902 and 1930.

XIII. THE DISPOSITION OF MERCURY AT TRAIL

Mercury is a liquid metal that evaporates at a relatively low temperature. The operating temperatures of Trail's hot cyclones, Cottrells, and baghouses were too high to efficiently collect mercury from its vapor.

To collect a substantial portion of the mercury from a flue gas, one needs to cool the gas to a reasonably low temperature, e.g., below 105 F (40 C). Scrubbing the gas with an aqueous solution provides this cooling. Much of the mercury captured at Trail was via cooling and cleaning flue gases in preparation for producing sulfuric acid. This preparation involved scrubbing with acidic solution, followed by mist elimination.

A. Mercury Recovery from Zinc Roaster Offgas

Zinc roaster offgas at Trail carried with it a substantial quantity of mercury and dust. Coarser dust was collected by first spinning the offgas in hot cyclone separators (550 F; 290 C). Over 95% of the remaining dust was then collected electrostatically in hot Cottrells (300 F; 150 C), for an overall dust collection efficiency of 99.5%. In 1962, Trail installed a baghouse (212 F; 100 C) to capture roaster flue dust, collecting 99.5% of dust exiting the cyclones.

Production of sulfuric acid at Trail began in 1916. By 1931, CM&S was scrubbing substantial volumes of its zinc roaster offgas, sufficient to convert over one-third of Trail's sulfur input to sulfuric acid. The purpose of scrubbing was to prepare the gas for production of sulfuric acid (Cobleigh, 1932, p 719). The cool scrubber environment, followed by mist elimination, likely captured at least 60% of the mercury prior to the acid plant (Steintveit, 1980, p 87; Dutrizac, 1979, p 207).

Hot Cottrell exit gas from the zinc roasters was split between four scrubbers (Glover towers) that used weak sulfuric acid to collect residual dust and metals as mud. Trail purged this mud into at least one pond called Glover Pond. In 1932, Cobleigh states that the acidic scrubber purge solution was consumed leaching zinc oxide (p 720). This practice appears to have been abandoned by 1934, when Hannay established the importance of avoiding

the addition of volatile impurities, particularly fluoride, to the zinc tankhouse electrolyte (Hannay, p 150).

Glover Tower exit gas was further scrubbed with water, then passed through a second Cottrell to eliminate mist. Both steps resulted in additional mercury collection. The gas was now sufficiently free from impurities for drying in preparation for producing sulfuric acid. The mercury-rich mud was captured by settling (Cobleigh, 1932, p 719; Anonymous, 1954, p 290). In 1977, the scrubber and mist eliminator solids were flushed into Glover Pond, as crudely shown in the upper left portion of Figure 20. The two wash water streams feeding Glover Pond in this figure carried the mud.

Figure 20 < ECY3-00000507>



A sample of mud taken from Glover Pond in 1990 assayed 18.0% Hg (Ball / Cominco, TECK 0110497). This mercury assay is likely correct. For example,

Electrolytic Zinc Company of Australia recovered 309,000 tons of zinc from concentrates containing up to 10 ppm Hg (1968 – 1970). The settled scrubber solids assayed between 10% and 40% Hg on a dry basis (Argall, 1971, p 33). The company dried the sludge from its scrubber-sludge pond, then fed it to a retort to recover flasks of mercury metal byproduct (3.4 tons/year).

B. Mercury Recovery from Lead Sintering-Plant Offgas

Until about 1940, lead sinter-machine offgas was passed through a humidifying flue, then through a Cottrell, followed by discharge to a 400-ft stack. A portion of the lead concentrate's mercury content likely reported to the solids collected during this flue humidification. The mercury-containing material was sent to yard storage, then returned to the second sintering operation (Huttl, 1938a, p 35). Recycling all of Hg-containing material back to sintering likely forced mercury to exit via the stack.

From 1940 to 1953, offgas from the sintering machines was still being humidified before dust collection in a Cottrell (90% dust removal). But now the Cottrell exit gas was scrubbed in packed cooling towers in order to provide dust-free gas for production of ammonium bisulfite. Tower wash water went to the Columbia River. The scrubber residue likely contained at least 60% of the mercury content of the lead concentrates fed to sintering. See the upper right portion of Figure 21. The remaining mercury entered the smelter's SO₂ absorption plant. This mercury would likely have split between the absorber stack, the ammonium sulfate product, and the acid plant.

In 1953, the sinter plant was upgraded to include wet-mix rotary drying of sinter-plant feed. (Wet mixing continued until the start of Kivcet smelting in 1997, when feedstock sintering was no longer required.) The relatively cool vent gas (350 F; 175 C) from the driers was cleaned in Doyle wet scrubbers. Doyle scrubbers, which are very efficient, likely captured as slimes most of the mercury vented from the driers. These slimes returned to the rotary driers; see Figure 21. The mercury would have eventually exited in the sintermachine offgas, then behaved as before, i.e., from 1940 to 1953. Scrubber slurry went to Sewer #7 until 1998 (TECK 0338974).

Figure 21. < ECY3-00000502>



Sewer #7 was the most contaminated of all the individual sewers at Trail, and represented the highest concentration and loadings of mercury, arsenic, and cadmium that went to the Columbia River (BCE 0001494 / Cominco, 1991, p 20).

C. The Quicksilver Material Balance for Mercury

This section examines a Cominco presentation titled *Chasing the Elusive* '*Quicksilver' at Trail Operations*. The subtitle of this presentation is *A Review* of *Mercury Control Improvements:* 1979 – 2002 (TECK 0338946, dated December 10, 2002). Included in the presentation are steps taken at Trail metallurgical operations from 1995 to 2002 to minimize outflow of mercury to the Columbia River (Teck 0338977):

- Installing a mercury pad
- Lining the lagoons
- Property-wide paving
- TMT (sulfide reagent) to precipitate Hg from Glover tower effluent
- Start-up of the Kivcet smelter
- Corrective action on spikes and spills

Included in the Quicksilver Presentation were approximate mercury inputs and outputs:

- Mercury input with concentrates: 73 tons / year
- Mercury recovered as calomel: 27 tons / year
- Mercury in residues and slag: 26 tons / year
- Unknown mercury: 20 tons / year
- Mercury in product elemental sulfur: 750 lb / year
- Mercury to stack and sewers: 440 lb / year
- Mercury in product sulfuric acid: 240 lb / year
- Mercury in fertilizer and other: 220 lb / year

It appears that these weight totals apply to 2002, i.e., the year the presentation was made. My observations on these mercury inputs and outputs are as follows:

<u>Mercury in feedstock concentrates</u>: Mercury input with concentrates in 2002 was 73 tpy (short tons per year), according to the Quicksilver. Based on the attached *Inputs and Distributions* spreadsheets, mercury input in concentrates in 2002 was 53 tons.

<u>Mercury output as calomel (Hg_2Cl_2) </u>: The Quicksilver Presentation reported that the Norzink scrubber captured 27 tpy Hg as calomel. Four findings related to this total are:

1) A Cominco patent applied for in 1995 (U.S. 5,601,795) stated that:

Levels of mercury in concentrate fed to the zinc roasters at the Cominco Ltd. plant in Trail, British Columbia, have been increasing over time due to an increasingly higher mercury content from ore concentrates of the Red Dog and Sullivan mines. This level of mercury results in more than 20 tonnes (22 tons) per year of crude calomel being formed.

The calomel in the patent assayed 74.3% Hg, so that the more than 22 tpy of calomel in the patent contained more than 16 tpy of Hg. The Quicksilver Presentation identified an average of 27 tpy of Hg as calomel, which indeed is more than the 16 tpy Hg in the patent.

2) One might reasonably expect that 98% of the 73 tpy Hg in concentrates fed to Trail made it to the Glover towers, and that the towers captured 65% of this mercury (Steintveit, 1980, p 87). Using these criteria, about 72 tpy Hg arrived at the towers, of which about 47 tpy reported to the Glover Pond. About 25 tpy Hg therefore reported to the Norzink scrubber (72 tpy minus 47 tpy). Trail's Norzink process captured most of this mercury (25 tpy), which is about that reported in the Quicksilver Presentation.

Overflow solution from Glover Pond was treated in the ETP (Effluent Treatment Plant).

3) In 1990, Magoon / Cominco (p 403) stated that this process (Boliden Norzink) results in the production of approximately 500 kg (0.5 tonnes) of impure calomel per year. Calculations summarized in the Inputs and Distributions spreadsheets indicate about 7.6 tpy Hg being recovered as calomel in 1989. It thus appears that there was a sharp increase in mercury input to Trail shortly after the 1990 publication date of Magoon's paper. This observation is consistent with the above patent's statement (1995) on the increasing mercury content in zinc roaster concentrates.

<u>Mercury output as residues and slag</u>: The Hg-rich residues in the Quicksilver Presentation were likely the total of those collected from Glover Pond and the ETP plant. In regard to Cominco's fumed slag output, the Hg content of both Trail's fumed and BF slags was insignificant, i.e., nil.

Unknown mercury output: When the Quicksilver Presentation compared mercury in with mercury out, an average of 20 tpy was missing. Difficulty in sampling mercury input to Glover Pond may well have resulted in this discrepancy. Mercury is readily reduced to metal, which can form dense Hg agglomerates. Accurately sampling ETP plant slurries and filter cake

containing isolated high-density particles of mercury would require substantial expertise. An unknown but possibly significant portion of the missing mercury may have volatilized.

Sampling ETP clarifier / thickener overflow exiting to the Columbia would likely have been straightforward. Furthermore, in the absence of foaming, dense metallics are unlikely to overflow.

The discussion above indicates that 47 tpy Hg reported to Glover Pond in 1992. This estimate corresponds to the Quicksilver Presentation total of unknown Hg (20 tpy) plus residue Hg (26 tpy).

<u>Mercury output to elemental sulfur</u>: Elemental sulfur is a byproduct of Trail's autoclaving zinc concentrate. Zinc sulfide oxidizes in aqueous solution to produce zinc sulfate electrolyte and elemental sulfur. About 750 lb of mercury per year was contained in Trail's elemental sulfur output, according to the Quicksilver Presentation. This quantity of Hg is small compared to Hg input from concentrates.

Mercury contained in sulfuric acid product: About 260 lb of mercury per year was contained in Trail's sulfuric acid output, according to the Quicksilver Presentation. Acid output, when protected by the Norzink process, assayed 0.6 ppm Hg (TECK 0340694). Assuming about 400,000 tpy acid output containing 0.6 ppm Hg, contained mercury calculates to 240 lb. The quantity of Hg to acid is indeed small when compared to Hg input from concentrates.

<u>Mercury contained in fertilizer and other</u>: The Quicksilver Presentation stated that the annual mercury content of Trail's fertilizer output was less than 220 lb/yr. This quantity of Hg going into fertilizer is small when compared to Hg input from concentrates.

Mercury output to stack and sewers: About 440 lb of mercury per year reported to stack and sewer, according to the Quicksilver Presentation. In 2002, mercury loss to stack, the Columbia, and Stoney Creek, via the *Inputs and Distribution* spreadsheets, as reported by Cominco, totaled 340 lb. These two values are reasonably consistent, when considering that the Quicksilver Presentation referred to averages.

<u>Mercury Input</u>: In 1992, Cominco Research wrote that *Hg inputs to the roasters in zinc concentrates are projected to be about 40 t/y* (44 short tons /

year). Because the autoclaves received somewhat less than 25% of the total zinc concentrate input, total projected mercury input from zinc concentrates was likely about 55 tpy. Our *Inputs and Distribution* spreadsheets show 42.7 tpy in zinc concentrates, respectively (1992). The spreadsheets therefore indicate that Trail's zinc roasters were fed more mercury than anticipated by Cominco Research in 1992.

D. Opinions from Section XIII

Opinion #39: For about eight decades, an unknown tonnage of mercury-rich mud collected from Trail's roaster-gas scrubbers and mist eliminators was stored, rather than directly discarded into the Columbia River.

Opinion #40: Prior to 1940, the mercury content of Trail lead concentrates reported to the stack. After 1940 and at least until 1998, at least half of lead concentrate mercury content reported to Sewer #7, which discharged to the Columbia. The remaining mercury reported to the absorber stack, the ammonium sulfate product, and the acid plant.

Opinion #41: The mercury content of Trail's fumed slag and BF slag waste was insignificant.

Opinion #42: The unknown whereabouts of the 20 tpy Hg reported in Trail's Quicksilver Presentation may have been due to difficulty in sampling inputs to Glover Pond. An unknown but possibly significant portion of the missing mercury may have volatilized.

Opinion #43: The quantity of mercury in byproduct sulfur, sulfuric acid, and fertilizer was small compared to Hg input from concentrates.

XIV. THE MODERNIZATION OF TRAIL: 1979 to 1991

By the early 1970s, it was apparent that Trail operations were aging and needed upgrading. Looking back, Charlie Sutherland (a senior Cominco engineer) observed that in 1970 economic and environmental considerations called for updated technologies. Sutherland's comments included the following observations (1988, p 86):

The many previous years of operation with steadily increasing capacity had seen continuing change in processes and in equipment, but many of the plants were aging and becoming increasingly expensive to operate. [In 1970], it was clearly necessary to regenerate the plants with the most efficient technology in order to restore the competitive position of the Trail

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smelter and also to bring it into conformity with stringent new standards in plant hygiene and the environmental impact.

The need to meet new environmental standards became particularly apparent when the Water Investigations Branch of the B.C. Ministry of Environment (B.C. MoE) published in two phases (1977 and 1979) the *Kootenay Air and Water Quality Study*. These reports detail the types and volumes of liquid wastes discharged into the Trail operations' sewers, and thence primarily into the Columbia River. Refer below to Section XV (The Sewers) for details.

In June 1978, the daily lead and zinc outputs from Trail were 425 and 625 tons, respectively. Fish wrote that much of the lead smelter was essentially 40 to 50 years old, dating back to the 1930s when lead BF slag fuming was implemented. There had been no major lead plant renovation for 38 years. *Cominco would have to spend millions more over the next decade if present provincial and federal government proposals for effluent and emission standards became law* (Fish, 1978, pp 34-36).

Modernization projects were of particular importance for minimizing transfer of As, Cd, Hg, Pb, and Zn to the Columbia River and Stoney Creek.

A. The Effluent Treatment Plant (1981)

The plant (ETP) was originally designed to treat contaminated water from lead and zinc operations by liming. An exception was Sewer #7, which carried strongly acidic solution from lead sinter-plant offgas cooling and scrubbing to the Columbia River until 1998. In the ETP, neutralization with lime generated a precipitate that was recovered by thickening. Neutralized thickener overflow liquor carried what was not precipitated, which flowed by sewer to the Columbia River.

Figure 22 shows the ETP thickener under construction. The thickener separated most of the solids away from liquid by decantation. Pulp density of the thickener underflow solids was maximized by recycling a major portion back to neutralization. A portion of the thickened sludge was either returned to the smelter or stored on site. About 18,500 tons of ETP sludge were produced from 1986 through 1990, of which about 5,400 tons were recycled (Cominco, 1991, TECK 0360275).



Figure 22. Construction of the effluent-treatment-plant thickener to collect heavy-metal precipitate from waste water (Fish, 1981, p 52)

Over the following decades, Trail 1) continued to improve the efficiency of metal precipitation in the ETP plant, 2) implemented process modifications to create less waste per ton of feedstock, 3) routed additional plant discharge streams to ETP feed, 4) expanded ETP capacity, 5) captured plant runoff, 6) added ferric iron to increase capture of arsenic, and 7) added TMT (trimercapto-s-triazine trisodium salt) to increase capture of mercury.

By 1991 there were five major sources for effluent feeds to the ETP: lead smelter, zinc operations, refinery (including refinery scrubber and silver refinery cooling water), copper products, and No. 13 Lagoon. The lead smelter, zinc operations, and copper products accounted for 97% of ETP sludge production: 34%, 40%, and 23%, respectively (Cominco, 1991, TECK 0369274).

Problems related to the ETP plant included the following:

- Mercury entering the ETP behaved inconsistently, in that this impurity occasionally passed through the ETP into the Columbia River (Cominco, 1997, TECK 0113293). Research was therefore undertaken to correct this problem, which likely resulted in the use of TMT sulfide reagent to more completely precipitate the mercury.
- The majority of the precipitated solids were put into storage due to difficulties in finding a suitable means to process them at Trail. This growing stockpile had its own set of environmental problems (Cominco,

1991, TECK 0369266). By 1995, the stockpile of ETP sludge (28% Zn) had grown to at least 41,000 dry tons (Cominco, 1995, TECK 0341989).

- The high mercury content of ETP sludge restricted its treatment through the roasters, and created an environmental concern over the ETP sludge stockpile (Cominco, 1991, TECK 0369275). Mercury content of ETP sludge inventory in 1991 was about 0.15% (Cominco, 1991, TECK 0369283).
- An unusual feed input could cause settling problems in the clarifier. A major clarifier upset could cause a spill situation to the Columbia River (Cominco, 1990, TECK 0359487).
- The flow of effluents to the ETP increased far beyond its design capacity. This high loading resulted in process upsets which adversely affected treated effluent quality (Cominco, 1991, TECK 0309266).

Condensed water purge from the Kivcet gas scrubber passed through an SO₂ stripping tower before being pumped to the effluent treatment plant.

B. Modernization of the Zinc Refinery (1981)

The principal environmental benefit of modernizing the zinc refinery was minimizing both the potential for spills and the likelihood that any spill would leave the plant.

C. Boliden Norzink Process (1981)

To meet sulfuric acid quality standards, it became necessary to remove mercury from the sulfur dioxide gas before it entered the sulfuric acid plants. The Boliden Norzink process reacted mercury-contaminated pre-scrubbed gas with recirculating solution of mercuric chloride. The mercuric – mercurous chloride couple captured most of the mercury vapor and mist that had passed through the Glover Tower and the mist eliminators.

The result was an impure mercurous chloride byproduct (calomel), most of which was inventoried. The mercury content of the sulfuric acid product was decreased to 0.5 to 0.7 ppm Hg, a level equivalent to about 1.5% of the total mercury input to the roasters (Magoon / Cominco, 1989, p 219).

D. Electrolyte Purge Recycle (1981)

Trail installed a pipeline to carry stripped zinc electrolyte to the fertilizer plant at Warfield for use in manufacturing phosphoric acid. A purge of zinc solution was necessary to control the magnesium content of the electrolyte (Fish, 1981, p 52). However, the addition of stripped electrolyte to the fertilizer circuit proved to have an unexpected deleterious effect on product grade. A new clarifier was constructed in 1984 to allow for increased consumption of stripped electrolyte in the fertilizer operation (ECY-000558).

E. Halide Leach Plant (1982)

Zinc oxide fumed from BF slag is high in halide content, e.g. chloride and fluoride, which causes problems during zinc electrolysis. This fume therefore was leached for its zinc content separately from the zinc oxide derived from roasting zinc concentrate.

To minimize process constraints associated with halides, Cominco built a plant in 1982 to remove halides from fume ZnO. Before leaching with spent electrolyte to extract zinc, the fume was leached with soda ash solution. Soda ash selectively dissolved most of the halides, along with a portion of the arsenic, cadmium, and thallium. The upgraded oxide dust was then leached in a single circuit with spent electrolyte, along with ZnO roasted calcine.

The halide waste liquor from the soda ash leach discharged to the Columbia River. This filtrate was high in thallium, cadmium, and arsenic; therefore, Cominco developed a means to treat this effluent. Implementation was delayed until it could be confirmed that the Kivcet smelter could handle the output metals (Cominco, 1997, TECK 0113262).⁶

F. Copper Products Plant (1989)

An improved copper products process reduced copper and arsenic effluent loadings (TECK 0068596).

With respect to arsenic, the Copper Products Plant is important. The inputs, operation, and capacity of the Specialty Products Plant and Copper Products

⁶ I do not know whether the Kivcet furnace was eventually able to recycle metals recovered when treating rather than discarding the halide-leach waste liquor.
Plant dictate what happens to the arsenic stockpile. The Kivcet smelter was not expected to affect the arsenic stockpile (Cominco, 1995, TECK 0095487).

In 1989, about 500 tonnes of arsenic entered the sinter plant. This arsenic ended up distributed between the silver refinery dust (\approx 310 tons), softening slag (\approx 210 tons), waste slag (\approx 22 tons), and product copper matte (\approx 11 tons). Subsequent processing of the refinery dust and softening slag produced arsenical lead product (Larouche / Cominco, 1989, pp 103-109).

Trail also produced high-purity arsenic products for the electronics industry, as well as copper arsenate for wood treatment. Arsenic oxide from treatment of Betts process anode slime provided the feedstock for electronic products. For details, see Hirsch / Cominco, 1980, p 360.

The two raw materials used to produce copper arsenate were copper sulfate (derived from copper matte) and high-As dust. The arsenic-rich dust came from the silver refinery (fumed off when processing Betts slimes), and from rotary-furnace rejection of arsenic and antimony from lead bullion (Davies, 1988, ECI-000513, Set #7). Test samples of copper arsenate were planned for shipment to a customer in 1991 (Ball, 1990, TECK 0110486).

Effluent from the copper products plant resulted in spikes of copper and arsenic reporting to the ETP (Cominco, 1997, TECK 0113291). Installing a cyclone on the copper sulfate drier vent was expected to provide a significant reduction in copper input to the ETP.

At Trail, more arsenic may be received in feedstocks than can be sold in product. Arsenic fuming from antimonial lead alloy furnaces can be recovered in a baghouse, then fused to a slag which is stockpiled in a special protected area.

G. Thallium Removal Plant (1989)

In 1991, thallium (TI) input to Trail metallurgical operations was about 50 tons per year. Shutting down the Sullivan mine decreased Trail's thallium input by 65%. (Cominco, 1995, TECK 0095485). About 1 tpd of zinc dust precipitated thallium, nickel, and cadmium from spent cadmium solution. Expected output was 200 to 300 tons/year of thallium-nickel residue assaying 10 to 20% TI. This residue was then to be refined in the new cadmium plant (Cominco, 1991, TECK 0337422).

The thallium removal plant improved the efficiency of thallium removal from process waste waters. No details were found on how these improved efficiencies were attained, or on the magnitude of these efficiencies (Cominco, 2007, Teck 0058577).

A disadvantage of using lime in the ETP was the inability of this reagent to precipitate thallium (Cominco, 1995, TECK 0341989). Thallium, like sodium, forms a soluble hydroxide, but like mercury, forms an insoluble sulfide.

Historically, Trail discharged about 20 tons of thallium per year to the Columbia River; the average in 1997 was about 8 tpy (D'Odorico / Cominco, 1997, TECK 0104762). Cominco examined in some detail the feasibility of producing thallium nitrate and thallium dichromate byproduct specialty chemicals (Knoerr / Cominco, TECK 0700834). Mr. Knoerr noted that current storage facilities were nearing capacity.

H. Elimination of the Electrolyte Purge Discharge (1990)

Elimination of electrolyte stripping discharge resulted in reduced zinc effluent loading to the Columbia River (TECK 0068596). This development was a major improvement, e.g., in the early 1970s, the discharge rate of acidic 18 gpl Zn stripped electrolyte was approximately 35,000 gallons/day; an equal quantity was converted to fertilizer micronutrient.

A means for productively consuming zinc tankhouse electrolyte purge had been developed at Trail in 1947. One added aqueous ammonia to the stripped electrolyte, cooled, then added ammonium bisulfite. A complex of zinc ammonium sulfite precipitated, which was returned to the roasters (King, 1950, p 2246). This method of recovering zinc from the electrolyte was apparently abandoned.

I. Collection and Treatment of Surface Water Runoff (1993)

A drainage control system routed storm water and washdown to the ETP, which involved paving and guttering a large area of the site. Traffic patterns were altered to keep industrial vehicles on site, and to limit exposure of the plant site to light vehicles (Cominco, 2007, TECK 0058578).

J. Indirect Heat Exchanger in the Lead Smelter (1994)

Installation of an indirect heat exchanger in the lead smelter separated process water from cooling water, i.e., a closed-cycle gas cooling system. The result was reduced levels of mercury and other metals discharged into the Columbia River via Sewer #7 (Cominco, 2007, TECK 0058577).

K. Effluent Treatment Plant Lagoon (1994)

Collection systems for storm water were upgraded, providing sufficient surge capacity to maintain a reasonable and steady flow to the ETP plant (Cominco 2007, 0058578).

L. TMT Addition for Mercury Precipitation (1995)

TMT is an organic reagent that contains sulfide. Cominco added TMT to the first tank in the ETP plant to precipitate mercury as its insoluble sulfide (ECI-001834).

M. Treatment of Copper Matte Granulation Water (1996)

Water used to granulate copper matte discharged directly to the Columbia River prior to 1996. This water contributed to effluent toxicity due to cadmium content. A pumping system was therefore installed to deliver this waste to the ETP (Cominco, 1997, TECK 0113292).

N. Eliminating Slag Discharge to the Columbia River (1996 - 1997)

A closed-circuit granulation and dewatering system to collect all of the slag was scheduled for construction (Kenyon, 1995, ECY-00968). In 1996, granulated fumed slag slurry was diverted to a collection pond; this diversion was completed in 1997 (Cominco, TECK 0715785). Discharge conveyers were installed so that the slag could be trucked to containment pads. The result was a 99.5% reduction of slag particulate loading of the Columbia River (Cominco, 1996, TECK 1087693; Cominco, 1997, TECK 0113261).

Cominco found a use and a market for its slag, which was supplied to several cement plants as a key ingredient to manufacture Portland cement (Kenyon, 1998, p 549).

O. Roof Drains and Perimeter Drainage (1997)

Plant modifications were targeted for completion in 1997 to divert roof and perimeter drainage, which can be contaminated, to the ETP rather than to *soakaways* (Cominco, 1997, TECK 0113293). Research was therefore undertaken to correct this problem.

P. Start-up of the Kivcet Smelter (1997)

In 1997, Trail's Kivcet lead smelter was commissioned, and became fully operational in 1999 (Report by G3 Consulting, 2001, CCT1 000625). Cominco had initially attempted to use the QSL continuous lead smelting process. The QSL process was unsuccessful in handling feedstocks that were very high in residue, rather than sulfide, content. Blast-furnace smelting continued to operate during start-up of both the QSL and Kivcet processes.

Kivcet smelting replaced the sinter plant, the blast furnaces, and the slag fuming furnaces with new technology to produce lead bullion. Kivcet smelting integrated the various smelting steps to substantially decrease dust evolution. Fugitive emissions were also decreased, especially those associated with sintering BF feed. Sewer #7 was eliminated.

Cominco summarized these improvements in its August 1997 <u>Effluent</u> <u>Management Plan</u> (TECK 0113291); see Figure 23:

The new lead smelter...will achieve a major reduction in dust emissions, which can impact the river directly as fall out and via surface runoff. It includes a closed circuit slag granulation system that eliminates any discharge of slag to the river. A fourth sewer (07 sewer) becomes redundant, as there is no need for gas scrubbing [of sinter-plant offgas]... In addition, the open storage areas associated with the old plants will be eliminated so that spills historically caused by snow melt and precipitation will be prevented. The new smelter is expected to be in full production by the second half of 1997.

Successful start-up of the Kivcet process decreased stack emissions of particulate matter, lead arsenic, mercury, fluoride, and SO_2 by 68 to 98% (Cominco, 2007, TECK 0058578).



Figure 23. Trail's Kivcet furnace (Ashman, 2000, p 175)

Processing of stockpiled materials: Beginning in 1983, the lead smelter could no longer keep up with processing the zinc leach residue, which had to be stockpiled (Werniuk, 2000, ECY3 00000807); *from a business point of view, it is preferable to minimize inventories so as to improve the timing of metals recovery* (de Groot / Cominco, 2000, p 315). By 1999, continuing to 2005, residue treatment was again in balance with production from zinc operations (Ashman, 2000, p 183; Heale, 2008, p 54). Sufficient fuming capacity was also available to process stockpiled BF slag (Heale, 2008, p 54).

The Kivcet smelter was expected to consume the zinc residue stockpile by 2010 (Cominco, 1995, TECK 0095486). The furnace also has the capability of consuming contaminated soil (Cominco, 1995, TECK 0095489). A key, as always, was economic viability.

Handling of Kivcet offgas: Furnace offgas passes through a boiler, Cottrell (590 F; 310 C), a spray tower (150 F; 65 C), then to a packed cooling tower (65 F; 19 C), prior to the acid plant (Ashman, 2000, p 177). Dust caught by the boiler and the Cottrells is recycled back to the Kivcet charge burners.

At least 60% of offgas mercury content thus would likely be captured prior to the acid plant, with most of the balance recovered as mercurous chloride via

Norzink scrubbing. Condensed scrubber water is stripped of its SO_2 content, then sent to the ETP.

Q. Elimination of Sewer #7 Discharge (1998)

Sewer #7, which discharged to the Columbia River, carried strongly acidic solution from lead sinter-plant offgas cooling and scrubbing, which in 1977 included 45% of the Pb, 40% of the Cd, and 10% of the Hg discharged from the Cominco complex. This sewer was the only one (of 12) that was not renovated in the early 1980s to flow into the ETP plant.

Sewer #7 continued to handle scrubbing water from ammonia absorption of SO₂ from sinter-plant offgas. Even though Sewer #7 was the most highly contaminated of all the individual sewers, its contents continued to flow to the Columbia River for over a decade after the other sewers had been diverted to the ETP plant. For further details, refer to Section XV (The Sewers).

R. Opinions from Section XIV

Opinion #44: Filtrate waste from the Halide Leach Plant was high in thallium, cadmium and arsenic content. A procedure to remove thallium, cadmium, and arsenic from halide leach effluent was developed at Trail, the implementation of which awaited demonstration that the Kivcet smelter would be able to handle the thallium, arsenic, and fluoride.

Opinion #45: The mercury content of material fed to the Kivcet furnace was efficiently captured by water cooling / scrubbing, followed by Norzink treatment. Mercury-containing Kivcet feed materials included lead concentrates and ETP sludge.

XV. THE SEWERS

Liquid and slurried solid wastes were discharged, primarily into the Columbia, using sewers; see Figures 24 and 25. In Figure 24, effluents can be seen discharging into the Columbia River in the middle of the left side of the photograph.



Figure 24. Discharge of effluents from Trail metallurgical sewers into the Columbia River in 1927 (B.C. Archives)



Figure 25. Cominco Metals slag discharge from Sewer #1 on the west bank of the Columbia River just upstream from the Highway 3 bridge (Nener, 1992, p 4,TECK 0715504)

Recall from Section XIV above that the B.C. MoE published in two phases (1977 and 1979) the *Kootenay Air and Water Quality Study*. These reports provide details on the contents of the sewers that carried Trail's wastes into the Columbia River and Stoney Creek. Phase 1 also provides useful process flow diagrams (Figures 8-8 through 8-13). Without Cominco's full cooperation, I doubt that such clear and professionally prepared diagrams would have been prepared.

A significant shortcoming of the B.C. MoE Phase 1 Study was that the smalldiameter tubing used for sample collection (1972 to 1975) did not achieve representative sampling of suspended material.

The results reported for total constituent are probably not accurate, and... remarks will apply mostly to results from dissolved constituents (1977, p 32).

Sewer sampling procedures used in the B.C. MoE Phase 2 Study were much improved.

The only metals entering Stoney Creek that are accounted for in this report are mercury and zinc. Mercury was in Trail's sulfuric acid used to produce fertilizer. Zinc electrolyte byproduct was delivered to the fertilizer plant as a source of both sulfuric acid and zinc micronutrient.

A. Findings on the 12 Sewers, as Detailed in the B.C. MoE Phase 2 Study

- <u>Sewers #1, #3, #4, #9, and #10</u> outflows, which discharged into the Columbia River, were relatively uncontaminated. These effluents included indirect cooling water, overflow from the lead BF slag pond, wash-down water, solution containing tellurium from processing Betts slimes, and nitrate liquor from precious-metal refining. These five sewers combined accounted for 4% of total lead discharged from Trail operations in 1977.⁷
- <u>Sewer #2</u> flushed fumed slag to the Columbia River using cooling water from the lead BF cooling jacket. Granulated and blast furnace slag produced by smelting lead at Trail included the following properties:

⁷ The percentages of total metal discharges to the river for each metal carried in each sewer in 1977, as presented in the B.C. MoE Phase 2 study, were calculated by Environmental Control, Cominco Ltd., at Trail.

- 1. Typical specific wet weight range of fumed granulated slag: 117 to 130 pounds per cubic foot (pcf), with in excess of 180 pcf occasionally recorded (Cominco, 2007, TECK 0058571). Fumed slag at Trail was, to my knowledge, always granulated.
- 2. Fumed slag is coarse- to medium-grained sand-sized particle that is black in color and has the appearance of obsidian (Cominco, 2007, TECK 0058572).
- Up to 1% of the granulated slag consisted of fine particles (minus 150 micron) that can break into an eggshell- and needle-like morphology. These fines remain suspended in the granulation water for extended periods (Cominco Research, 1991, TECK 0338636).
- Grain size of fumed slag is well-sorted sand-sized particles containing 0.1 to 0.3% of fines having diameters less than 75 microns (Cominco, 2007, TECK 0058572). See Figure 26 in Section XV-B below for additional details.
- 5. Composition of Trail's granulated slags from lead smelting blast furnace and fumed varied in composition. Reasons for this variation included:
 - Upgrading of operating practice with experience over the years.
 - Variations in the ratio of the major gangue constituents.
 - Variation of slag composition as a function of particle size.
 - Variation of slag composition from start to finish during granulation.
- 6. The silica (SiO₂) concentration of Trail's fumed slag was reported in 2007 as about 31% (Cominco, TECK 0058572). Silica content recorded in historical analyses of the fumed slag (1931 1994) ranges from 26 to 30% SiO₂. See Spreadsheet 5 for Trail fumed slag analyses found in literature and documents. Typical SiO₂ in 1992 was 26 to 28% (Cominco, TECK 0338545). Silica analyses in BF slag in 1922 and 1923 were 15.8 and 18% respectively (Spreadsheet 5). Trail's lead and copper blast furnace slag, to my knowledge, was granulated beginning in the early 1900s.
- 7. The lime (CaO) concentration of Trail's fumed slag was reported in 2007 as about 15% (Cominco, TECK 0058572). Lime content recorded in historical analyses of the fumed slag (1937 1994) range from 9 to 17% CaO. See Spreadsheet 5 for Trail fumed slag analyses found in literature and documents. Typical CaO in fumed slag in 1992 was 14 to 16% (Cominco, TECK 0338545). Lime in BF slag in historical analyses between 1922 and 1925 was 6 to 10% (Spreadsheet 5).

- The iron (Fe) concentration of Trail's fumed slag was reported in 2007 as about 30% (Cominco, TECK 0058572). Iron content recorded in historical analyses of the fumed slag (1937 – 1994) ranges from 31 to 37% Fe. See Spreadsheet 5 for Trail fumed slag analyses found in literature and documents. Typical Fe in fumed slag in 1992 was 33 to 34% (Cominco, TECK 0338545). Iron in BF slag between 1922 and 1925 in historical analyses was 31 to 33% (Spreadsheet 5).
- Alumina (Al₂O₃) in a 1923 analysis in BF slag was 3%. Fumed slag in 1954 was 8.5% Al₂O₃. Typical alumina in fumed slag in 1992 was 3 to 5% (Cominco, TECK 0338545).
- Analyses of lesser fumed slag constituents reported by Cominco in 2007 (TECK 0058572) are as follows: zinc 2.6%; lead 0.1%; arsenic 0.01%; cadmium 0.001%; antimony 0.003%; copper 0.5%; potassium 0.6%; magnesium 0.5%; manganese 0.5%; and sodium 1.1%.
- Zinc variability in Trail's fumed slag was 2.3 to 3.4% (Spreadsheet #5). Typical zinc in 1992 in fumed slag was 2.5 to 3.5% (Cominco, TECK 0338545). Blast furnace slag (unfumed) was much higher in zinc content (14 to 22% between 1921 and 1930; see Spreadsheet #5).
- 12. Lead variability in Trail's fumed slag was 0.03% to 0.20% (Spreadsheet #5). Blast furnace slag (unfumed) was much higher in lead content (1.2 to 2.4% between 1921 and 1930; see Spreadsheet #5).
- Arsenic variability in Trail's fumed slag between 1984 and 1995 was 0.008% to 0.017% (Spreadsheet #5). During the 1920s, blast furnace slag reportedly contained about 0.15% As (Spreadsheet 5).
- 14. Cadmium variability in Trail's fumed slag was <0.0006% to 0.002% (Spreadsheet #5). Assays taken in 1991 of fumed slag granules during tapping varied from 0.001 to 0.023% Cd (Cominco Research, TECK 0338651). Typical cadmium in 1992 in fumed slag was 0.002% (Spreadsheet #5). During the 1920s, blast furnace slag reportedly contained about 0.01% Cd (Spreadsheet 5).
- 15. An additional complication is that the analysis of slag produced during fuming a batch process varies not only from start to finish, but also depends on particle size; see Figure 26. For example, the lead content of the fine slag granules (smaller than 150 microns) ranged from 1.2% Pb during the first slag tap to 0.05% Pb in the last slag tap. The overall slag lead content (average of all particle sizes) was reasonably constant (0.02 to 0.04%). See Cominco Research document TECK 0338651 (1991) for additional details.

- 16. Mercury is so volatile at slag-granulation temperatures that mercury is not a significant constituent in granulated slag. This wording is mine, but it reflects the gist of Cominco's 2007 finding (TECK 0058572).
- 17. The granulated slag particles are vitrified into a glass-like matrix (Cominco, 2007, TECK 0058572).

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Particle Size Distribution of Fuming Furnace Slag for a Blend of Start, Mid and End Taps from Several Tapping Cycles.

Particle Size (um)	Screen Size	Distribution (%)
+2000 gronules	+10	9.8
425 - 2000 coarse	+40 -10	75.4
212-425 med for	+70 -40	12.6
150-212 Fine	+100 -70	1.2
75 - 150 + my fine	+200 -100	0.67
45 - 75 coarse -45 medium	+ 325 - 200	0.14
-45 medium 5	-325	0.18

Assays of Start, Mid- and End-tap Water-granulated Slags from Several Tapping Cycles

Sample	Particle Size	Assay (%)							
Composite		Pb	Zn	Cd	Cu				
		400 ppm	40,000 ppm						
Start-tap	All Size Compo	0.04	4.0	0.023	1.19				
	-150 um	1.2	3.8	0.003	1.4				
Mid-tap	All Size Compo	0.02	3.4	0.006	1.13				
	-150 um	0.06	3.9	0.001	1.4				
End-tap	All Size Compo	0.04	3.5	0.005	1.05				
•	-150 um	0.05	3.7	0.001	1.3				

From: Cominco Research. 1991. Metals-Related Environmental Assessments of Disposal Options for Fuming Furnace Slag

Figure 26. Fumed slag particle size distribution and analyses at start, middle, and end of tapping, from a Cominco document on slag disposal options (1991, TECK 0715529)

• <u>Sewer #5</u> mainly carried clarified aqueous effluent from lime neutralization of effluent generated when scrubbing offgas from the rotary driers in the lead sintering plant. This sewer, which discharged to the Columbia River, also carried aqueous waste generated when humidifying sinter-machine exhaust gas, as well as floor washings. Refer back to the Settling Tank on the right side of Figure 21.

Also included were floor washings and indirect cooling water. Sewer #5 carried 33% of the cadmium, 10% of the zinc, 2% of the lead, and 2% of the mercury discharged from Cominco in 1977.

- <u>Sewer #6</u> carried effluent to the Columbia River from scrubbing zinc melting furnace offgas, which likely included vapor from a zinc ammonium chloride melt covering. Also included was indirect cooling water, and various washdown and runoff solutions from the zinc sulfide leaching plant. Sewer #6 effluent contained about 9% of the zinc, 4% of the lead, and 2% of the cadmium discharged from the Cominco complex in 1977.
- <u>Sewer #7</u> carried strongly acidic solution from lead sinter-plant offgas cooling and scrubbing to the Columbia River. This sewer carried 45% of the Pb, 40% of the Cd, and 10% of the Hg discharged from the Cominco complex in 1977.
- <u>Sewer #8</u> also discharged into the Columbia River. This sewer primarily carried acidic stripped zinc electrolyte purge. Sewer #8 also carried effluent from zinc roaster gas scrubbing, plus clarified wash water from the Glover Tower and Cottrells. Also included were indirect cooling water, and various wash solutions This sewer carried major shares of the total Zn (88%⁸), Hg (43%), Cd (25%), and Pb (23%) that exited from Trail operations into the Columbia River.

The B.C. MoE Phase 1 Study stated that the stripped zinc electrolyte purge was 35,000 gal/day of liquor assaying 18 gpl Zn. The 35,000 gallons gal/day of 18 gpl Zn discharged in 1977 calculates to less than 10% of the total zinc (not including slag) sent to Trail's sewers that year. An equal quantity of stripped electrolyte went to the fertilizer plant to produce ZnMnS micronutrient (1977, pp 25-26). Total effluent volume from all sewers was 55 to 60 million gallons per day (1977, p 31).

⁸ The percentage of zinc reported as going to the twelve sewers appears to be greater than 100%.

• <u>Sewers #11 and #12</u> came from the Warfield fertilizer plant. These sewers contained most of the calcium sulfate (gypsum), phosphorus, ammonia, and fluoride discharged from the Cominco complex, plus 40% of the mercury and 4% of the lead.

Sewers #11 and #12 discharged into Stoney Creek, 600 meters upstream from the Columbia River, until mid-1978. They were then discharged via a submerged diffuser to the Columbia. However, the new line and diffuser encountered wear problems. While work was undertaken to overcome these problems, Sewers #11 and #12 continued to discharge into Stoney Creek (B.C. MoE Phase 2 *Kootenay Air and Water Quality Study*, 1979, p 51).

B. Rearrangement of Trail's Sewers in the 1980s

By 1985, there were five sewers (TECK 0617717); one, Sewer #7, was a holdover from the earlier days of 12 sewers. Descriptions of these sewers published in 1991 and 1995 include the following (BCE 0001475; TECK 0112310). A more detailed description of Trail sewer permitting history appears in Cominco, 2007, TECK 0058569.

 <u>Sewer I</u>: This sewer, which discharged to the Columbia River, collected effluent discharged from the Blast Furnace Pond, the old #2 Sewer, and the fumed slag launder. Most of the water in the Blast Furnace Pond was indirect cooling water. This sewer also carried yard runoff, and contaminated water from granulation of copper matte. Details on fumed slag particle size distribution and analyses, as provided by Cominco in 1991, appear in Figure 26 (TECK 0715529).

Sewer I was a significant contributor of Cu (15%), as compared to other sources. Considerably more metals were lost to the Columbia River via this source during slag tapping cycles (TECK 0112310).

 <u>Sewers II and III</u>: These two sewers, which discharged to the Columbia River, collected the cleaner portions of the process water from the balance of the metallurgical operations. Highly contaminated streams were piped directly to the ETP. Road and plant wash water passed directly into Sewers I, II, and III. A portion of contaminated property drainage was stored in a lagoon (#13) for eventual treatment in the ETP plant. A second lagoon (#12) collected contaminated runoff from roadways and material handling areas for eventual ETP processing. These two lagoons were also available to provide surge capacity, should the ETP go down for maintenance or for an operating adjustment.

In addition to carrying outfall solution from the ETP, Sewer III serviced the fume leach plant, pressure leaching, the zinc oxide plant, zinc electrolysis and melting, the lead refinery, and stockpile areas.

Sewer II was a minor source of As and Hg, a negligible source of TI (thallium), and a significant source of Cd (24%) and Zn (18%). It was a major source of copper (40%) and lead (59%); see TECK 0112310.

Sewer III was a minor source of As, but a major source of Hg (80%) and dissolved thallium (99%). Its Cd, Cu, and Zn content was similar to Sewer II; lead loading was lower (TECK 0112310).

Sewer IV: This sewer collected from the fertilizer plant and Stoney Creek (which flows into the Columbia), which received leachate from a variety of waste and residue landfills. See TECK 0112310, 1996. I understand that Sewer IV discharged into the Columbia River, and that problems encountered with a submerged diffuser in 1978 were rectified.

The 1996 assessment of metal sampling results, as prepared by the B.C. Environmental Protection (Kootenay Region), indicates that Stoney Creek was a major source of As (80%), Cd (52%), and Zn (61%). Most of the Cd and Zn, and half of the As, were in dissolved form, which suggests a groundwater source rather than surface runoff. By 1996, Cominco had discovered that groundwater was indeed seeping into both sides of Stoney Creek, resulting in contamination with Zn, Cd, and As. Work commenced to find a means to divert this outfall into the ETP plant (Cominco, 1997, TECK 0113262). This diversion was completed in 1999, reducing As, Zn, Cd, and ammonia loads to the river (TECK 0068599).

Additional details on mercury output from the fertilizer plant are provided in ECI-000896 and TECK 0079018. It appears that the phosphate rock (700 tons/day in 1989) was providing on the order of 1 tpy of Hg. The balance,

on the order of 0.3 tpy Hg, was dissolved in the sulfuric acid (which contained about 0.6 ppm Hg).

- 1. Cominco ceased producing phosphate-based fertilizer in 1994, which eliminated Warm Springs Mine (Montana) phosphate rock as a mercury source.
- 2. During 1988-89, Warm Springs rock was unusually high in mercury content. Note the spike in mercury discharged during this period into Trail's fertilizer operation's sewers, as shown in Figure 27.
- 3. Prior to installation of the Norzink process in 1981, the mercury content of the sulfuric acid was substantially higher than 0.6 ppm Hg, e.g., about 7 ppm Hg. See the attached Inputs and Distributions spreadsheets for details.



COMINCO LTD. TRAIL OPERATIONS Avg. Daily Discharge to Columbia River

Figure :

Figure 27. Mercury outfalls (1992 Trail Environmental Report; TECK 0079018)

- **4.** Figure 27 also indicates that even though the Norzink mercury removal plant went on line in 1981, it did not attain consistent mercury capture until 1984.
- 5. An unknown portion of the mercury entering the fertilizer plant stays with the fertilizer.

PBQ – Expert Opinion - 9/15/10

<u>Sewer #7</u>: This sewer, which discharged to the Columbia River, survived from the old sewer system. It continued to handle scrubbing water from ammonia absorption of SO₂ from sinter-plant offgas. Even though Sewer #7 was the most highly contaminated of all the individual sewers, its contents flowed to the Columbia River rather than to the ETP plant. Sewer #7 solution was saturated with SO₂, making individual treatment difficult. Its piping was specially constructed to resist corrosion (BCE 0001494, 1991, p 20).

By 1997, the Kivcet furnace was sufficiently proven to permit shutting down the blast furnaces, along with their sinter-plant feed-preparation facility (TECK 0338974). The Kivcet furnace produced sulfur dioxide of sufficient strength to feed a conventional acid plant, so ammonia scrubbing to concentrate SO_2 was no longer necessary. A difficult metalcontaminated waste was therefore no longer generated, leading to Sewer #7's demise in 1998.

C. Total vs Dissolved Metals, Primarily Discharged to the Columbia River

A substantial portion of the metals discarded by Trail, primarily into the Columbia, were solids; see Figure 28 below. The graphs provide average daily measurements of total and dissolved metal outfalls (Pb, Zn, Cd, As, Cu and Hg) for various periods between 1980 and 1996. Most of the lead and copper discarded to sewer were carried as particulates. A substantial portion of the cadmium and arsenic were dissolved. In regard to zinc, the graph is difficult to read. The graph for mercury outfalls compares metallurgical and fertilizer outfalls for 1980-96 (1997 Trail Effluent Management Plan; TECK 0113283).

D. Opinions from Section XV

Opinion #46: Without Cominco's full cooperation, I doubt that such clear and professionally prepared diagrams would have been prepared by the B.C. MoE, as published in Phase 1 of the *Kootenay Air and Water Quality Study* (1977).

Opinion #47: Figures 8-8 through 8-13 in the B.C. MoE Phase I *Kootenay Air and Water Quality Study* (1977) appear to depict with reasonable accuracy the relationship between Trail's metallurgical operations and its sewers.

Opinion #48: Cooling water that does not contact a plant process stream should carry very little of the metals in Trail's feedstocks when discarded into Trail's sewers.

In contrast, direct-contact cooling water can be expected to carry process constituents.



Figure 28. Average daily measurements of total and dissolved metals (Pb, Zn, Cd, As, Cu and Hg) for various periods between 1980 and 1996 (1997 Trail Effluent Management Plan; TECK 0113283)

Opinion #49: The B.C. MoE Phase 2 *Kootenay Air and Water Quality Study* (1979) tabulates total weights of Cd, Hg, Pb and Zn discharged into the Columbia from Trail metallurgical and fertilizer operations in 1977 (Table 23 on pp 169-72). These values, as provided by Cominco, are reasonably consistent with Cominco's 1980 data. Furthermore, these effluent assays are the best data provided from this period. I therefore have relied on these values.

Opinion #50: Prior to smooth operation of the Norzink mercury removal plant, a substantial portion of Trail's fertilizer-plant mercury effluent originated from mercury contained in the plant's sulfuric acid feedstock.

XVI. INPUTS AND DISTRIBUTIONS SPREADSHEETS

The attached Inputs and Distributions Spreadsheets include estimates of the weight of Pb, Zn, As, Cd and Hg originating from Trail's metallurgical operations from 1921 to 2005 discharged directly into either the Columbia River or into Stoney Creek. Insufficient data were available to make similar estimates of copper outfall. Most of these data used to prepare these estimates were provided by Teck Metals, various environmental authorities, and technical publications. This data proved to be reasonably internally consistent, and credible.

A. Metal Discharges, Primarily to the Columbia River: 1921 to 2005

Results are summarized in Tables 2 and 3.

B. <u>Sheet 1</u>: Lead Concentrate Analyses

Assays are provided for Sullivan and Red Dog lead concentrates. Average annual custom feedstock assays were not available; therefore Sullivan lead concentrate analyses were used to represent the custom feeds.

C. <u>Sheet 2</u>: Zinc Concentrate Analyses

Assays are provided for Sullivan, Pine Point, and Red Dog zinc concentrates. Average annual custom feedstock assays were not available; therefore Sullivan zinc concentrate analyses were used to represent custom feeds.

D. <u>Sheet 3</u>: Copper, Lead, Zinc and Cadmium Production

Estimates of Trail's copper, lead, zinc, and cadmium production (1921 to 2005) are provided.

	TABLE 2.	SUMMARY	OF NON-	SLAG DISC	HARGE	S, PRIMA	RILY 1	O THE C	COLUN	IBIA RIV	'ER	
	Lead	Zinc	Zn Di	scharges	Pb Dis	charges	As Di	scharges	Cd Di	scharges	Ha Di	scharges
	Prodn	Prodn	Outfall	Emission	Outfall	Emission		Emission			U U	Emission
Years			outun			the time peri	_		- and			
921-1930	1,055,428	607,794	6,437	12,811	1,478	4,098	73	310	27	76	17	39
931-1940	1,717,519	1,175,379	24.094	13,127	1,312	5,913	54	207	80	79	30	36
941-1950	1,812,032	1,479,263	36,560	10,286	4,025	3,434	94	186	120	79	45	29
951-1960	1,557,697	1,815,753	56,937	564	4,339	2,073	107	173	180	55	42	29
961-1970	1,794,879	2,079,828	65,217	646	5,000	2,389	102	166	186	57	42	27
971-1980	1,475,196	2,150,179	67,423	668	4,109	1,963	98	159	189	58	37	24
981-1990	1,180,700	2,595,000	19,500	890	1,500	1,500	70	200	160	100	13	34
991-2000	873,600	2,592,900	7,958	593	556	862	77	92	28	39	2	14
2001-2005	377,200	1,239,300	131	283	11	11	3	3	1	0.3	0.1	1
			1									
921-2005	11,844,251	15,735,796	284,222	39,868	22,298	22,215	677	1,492	972	511	227	234
				Slag Discharged	Pb in Slag	Zn in Slag	Cd in Slag	As in Slag				
			Years	, v		U U	Ū,		-			
			Tears		lotal tons for	or the time p	eriod					
			Tears		lotal tons for	or the time p	eriod					
			1921-1930	1,255,965	10tal tons f 32,469	or the time p 179,904	eriod 109	1,632				
								1,632 204				
			1921-1930	1,255,965	32,469	179,904 48,208 50,861	109 14 15	204 216				
			1921-1930 1931-1940	1,255,965 2,043,858	32,469 2,248	179,904 48,208	109 14 15 13	204				
			1921-1930 1931-1940 1941-1950	1,255,965 2,043,858 2,156,329	32,469 2,248 2,372	179,904 48,208 50,861	109 14 15	204 216				
			1921-1930 1931-1940 1941-1950 1951-1960	1,255,965 2,043,858 2,156,329 1,853,669	32,469 2,248 2,372 2,039	179,904 48,208 50,861 60,519	109 14 15 13	204 216 185				
			1921-1930 1931-1940 1941-1950 1951-1960 1961-1970	1,255,965 2,043,858 2,156,329 1,853,669 2,146,558	32,469 2,248 2,372 2,039 2,361	179,904 48,208 50,861 60,519 50,630	109 14 15 13 15	204 216 185 215				
			1921-1930 1931-1940 1941-1950 1951-1960 1961-1970 1971-1980	1,255,965 2,043,858 2,156,329 1,853,669 2,146,558 1,724,615	32,469 2,248 2,372 2,039 2,361 1,897	179,904 48,208 50,861 60,519 50,630 39,586	109 14 15 13 15 12	204 216 185 215 172				
			1921-1930 1931-1940 1941-1950 1951-1960 1961-1970 1971-1980 1981-1990	1,255,965 2,043,858 2,156,329 1,853,669 2,146,558 1,724,615 1,540,376	32,469 2,248 2,372 2,039 2,361 1,897 1,694	179,904 48,208 50,861 60,519 50,630 39,586 33,305	109 14 15 13 15 12 11	204 216 185 215 172 154				

E. <u>Sheet 4</u>: Estimated Feedstock Tonnage (1921 to 2005)

Estimated annual tonnages of Sullivan, Pine Point, and Red Dog feedstocks are provided.

F. <u>Sheet 5</u>: Blast Furnace and Fumed Slag Analyses

Typical BF (1921 to 1929) and fumed (1930 to 2005) slag analyses are provided.

G. Sheet 6: Estimated Metal Discharges in Slag to the Columbia River

Annual slag production is provided from 1921 to 2005.

H. <u>Sheet 7</u>: Production of Sulfuric Acid (100% Basis)

The primary basis used in Sheet 7 to estimate acid production was available acid-plant capacity. Acid output was based on plant capacity because published data on annual sulfur conversion at Trail were contradictory.

I. <u>Sheet 8</u>: Summary of Non-Slag Discharges, Primarily to the Columbia River, and Air Emissions

Emissions and discharge data are provided for Pb, Zn, As, Cd and Hg (1921 to 2005).

J. Sheet 9: Unaccounted or Inventoried Metals

The difference between the tonnage of feed inputs and the tonnage of (products + outputs + emissions) is material that is in inventory or unaccounted for.

Unaccounted-for material can arise from incorrect feed assays, incorrect feed weights, and undocumented material exiting from Trail's metallurgical facility, e.g., as product, river discharges, emissions, or theft.

K. <u>Sheet 10</u>: Measured Metals Emissions to Atmosphere

Emissions data span from 1980 to 2005. Prior emissions were not available, and therefore are factored estimates.

L. Sheet 11: Measured Metals Outfalls, Primarily to the Columbia River

Outfall data span from 1977 to 2005. Prior outfalls were not available, and therefore are estimated using criteria detailed in *Explanation of Spreadsheet Details*.

Zinc and mercury discharges from fertilizer operations are compared below to that from metallurgical operations. Depending on the time period, both the Columbia and Stoney Creek were utilized for mercury and zinc disposal.

The metallurgists sent mercury to the fertilizer plant dissolved in sulfuric acid. A portion of the zinc sent to the fertilizer plant for micronutrient went to waste.

The zinc outfall data show:

1977	4,800 tpy metallurgical, Sheet 11 cells J8 ar	1.3% from the fertilizer
1984	1,400 tpy metallurgical, Sheet 11 cells J15 a	4.4% from the fertilizer
1993	100 tpy metallurgical, Sheet 11 cells J24 a	31% from the fertilizer

The mercury outfall data show:

- 1977 0.88 tpy metallurgical, 1.6 tpy fertilizer, 64% from the fertilizer Sheet 11 cells Q8 and R8
- 1984 0.48 tpy metallurgical, 0.24 tpy fertilizer, 33% from the fertilizer Sheet 11 cells Q15 and R15
- 1993 0.44 tpy metallurgical, 0.15 tpy fertilizer, 27% from the fertilizer Sheet 11 cells Q24 and R24

M. <u>Sheet 12</u>: Arsenic Balance

Sheet 12 provides the annual input/output balance for arsenic.

N. Sheet 13: Cadmium Balance

Sheet 13 provides the annual input/output balance for cadmium.

O. Sheet 14: Lead Balance

Sheet 14 provides the annual input/output balance for lead.

P. Sheet 15: Mercury Balance

Sheet 15 provides the annual input/output balance for mercury.

Q. Sheet 16: Zinc Balance

Sheet 16 provides the annual input/output balance for zinc.

R. Explanation of Spreadsheet Details

Explanation of Spreadsheet Details provides the bases used to construct the spreadsheet.

S. Opinions from Section XVI

Opinion #51: Most of the information and data provided by Teck Metals, various environmental authorities, and technical publications were found to be reasonably internally consistent and credible.

Opinion #52: Estimated direct discharges to the river from Trail's metallurgical operations from 1921 through 2005 are summarized in Tables 2 and 3. Details appear in the *Inputs and Distributions Spreadsheets*.

PBQ – Expert Opinion - 9/15/10

Opinion #53: Annual data show variations due to non-quantified metal in inventory. Therefore 10-year averages are a better basis for data comparison.

Opinion #54: When preparing this expert report, annual acid-plant capacity appeared to be the best basis for estimating annual acid-plant production.

XVII.STANDARDS FOR OPINIONS

My opinions in this report are expressed to a reasonable degree of scientific certainty.

APPENDIX A: A TRAIL PLANT PROFILE - 1954

The May 1954 supplemental issue of *Canadian Mining Journal* featured *The Story of Consolidated Mining and Smelting Company of Canada Limited* (Anonymous). The *Smelting and Refining* section is a detailed, well written description of Trail operations. This description provides a footprint of Trail practice that is helpful in understanding and quantifying plant practice prior to beginning the plant's major modernization in 1979.

Key findings abstracted from this 1954 publication are as follows:

A. Sintering BF Feedstocks

 <u>Feed proportions to sintering</u> were guided by 1) the relative tonnage of lead bullion and zinc oxide fume, 2) the BF slag assay, 3) Ag, Sb, and As reporting to the bullion, and 4) fuel needs for proper sintering. Trail's wet-mix technique, used to prepare sinter-plant feed, blended moist zinc-plant leach residues with the other feedstocks. These various sinter-plant feedstocks are tabulated in Table A1. Dust collected from sintering was returned to wet mixing (p 242).

The 14% moisture wet mix was dried to about 7.5% moisture in rotary driers. Output was nodulized in a rotary drum (no external heating) to attain suitable strength and permeability for efficient burning off of sulfur on the sintering machines. Vent gas from the driers (275 F) was vented to Doyle scrubbers, then released via a stack.

Sulfur content in sinter feed was about 11.5% (p 237). The final sinter assayed 1.3% S (p 238). Sinter bed temperature was about 2000 to 2100 F.

- <u>Sinter plant feed</u> relative weights and assays are shown in Table A1 (p 237)⁹.
- <u>Granulated BF slag and coke breeze</u>, about 9% and 1.5% respectively, were added to the charge fed to the second stage of sintering (p 240).

MATERIAL			-					
	CHARGE	Pb	Zn	SiO ₂	Fe	CaO	Total S	H ₂ O
Sullivan Flotation Conc.	21.0	64.0	8.0	1.2	6.5	0.1	18.2	9.0
Custom Ores and Conc	19.0	48.6	7.5	13.0	6.3	1.0	17.0	
Calcine, Leached Residues	28.5	10.5	22.6	3.5	26.5	1.0	6.6	34.0
Fume, Leached Residues	9.5	30.0	10.1	4.0	12.5	2.0	9.0	30.0
Crushed Siliceous Ore	5.5	0.2	0.2	8.5	2.0	2.0	1.0	3.0
Crushed Limercck	7.5			7.0	0.7	52.5	_	3.0
Iron Concentrates	4.0	, 1.0	1.0	0.9	56.2	0.1	35.0	9.0

Table A1: Sinter-Plant Feedstocks (Anonymous, 1954, p 237)

- <u>Sintering machine dust, fume, and SO₂-laden gas</u> were first passed through a balloon flue, then to a humidifying chamber, then to Cottrells, then to SO₂ absorption using ammonia-rich solution. Cleaned gas vented to a 400-ft stack (p 241-242). Conditioning the dust to 4 to 6% moisture was key for its efficient collection in the Cottrells. Flue temperature was kept sufficiently high to avoid condensation of corrosive cake-forming moisture.
- <u>BF charge</u> consisted of about 85% sinter, plus pot-shell skulls, settler bottoms, and occasional lots of direct-smelting ore (p 242). The BF feed bins stocked 4000 tons of sinter, 1000 tons of furnace coke, and 500 tons of miscellaneous charge materials (p 243).

 $^{^{9}}$ The SiO₂ assay of Crushed Siliceous Ore is assumed to be 85%, not 8.5%. PBQ – Expert Opinion - 9/15/10

Sulfur content in the BF charge was minimized. Sulfur in the BF slag output was detrimental to subsequent zinc fuming. Sulfur also increased the rate of BF accretion formation (p 243).

B. Blast Furnace Slag

<u>BF slag</u> was adjusted to be as high in zinc as possible, typically 17% Zn (Table A2). Iron, lime, and silica were proportioned to give reasonable fluidity at reasonable temperatures (p 243). Lead content, which averaged about 2.5%, was not a concern; it was recovered during subsequent slag fuming. For key assays, see Table A2 (p 248).

Most of the BF slag was kept hot in preparation for fuming. A portion was granulated, then sluiced to a BF slag pond, where it was either reclaimed for the sinter plant, or to stockpile.

Table A2:	Representative Analyses of Metallurgical Products
	(Anonymous, 1954, p 248)

SINTERING AND FURNACE PLANTS

	Percent								
_	Cd	Cu	Pb	Zn	S	SiO ₂	Fe	CaO	Al ₂ O ₃
First Sinter	0.24	0.30	44.3	7.8	6.1	6.7	11.1	4.1	
Final Sinter	0.23	0.30	40.4	9.1	1.3	8.5	13.4	4.9	
Sinter Plant Flue Dust	1.7		59.9	1.1	12.5			<u> </u>	
Lead Blast Furnace Slag.		0.15	2.5	17.0	2.4	20.8	26.0	10.3	5.3
Lead Blast Furnace									-
Baghouse Dust			51.7	15.1	5.3	0.9	0.5	5.2	/
Fuming Furnace Slag		0 18	0.09	2.3	1.6	29,4	33.0	12.2	8.5
Fuming Furnace Fume			7.4	69.9	1.1	0.4	0.3	0.2	

DROSSING PLANT		Fercent					C	Ounces			Percent		
	Cu	Fb	S	As	Sb	Sn	Bi	Ag	Au	SiO ₂	Fe	CaO	
Bullion Dross. Copper Matte-	16	55	4.5	4.0	1.0	2.0	0.02	50	0.03		3.0	·	
Speiss	55	20	12	3.0	1.0	0.05	<0.005	60	0.02	0.4	0.5	0.1	
Lead Anodes	0.04	98.3	3 —	0.30	1.0	0.003	0.06	80	0.10	—			

- <u>BF offgas</u> was first cooled countercurrently by water sprays and dilution air in a tower. A portion of the dust collected at the base of the tower, where it was removed by dragline. The cooled gas (250 F) then entered a baghouse for dust recovery, followed by discharge of the cleaned gas through a 284-ft stack. The recovered dust returned to the sintering plant (pp 243-245).
- <u>Copper-rich dross</u> was rejected from the BF bullion by cooling. This dross (16% Cu; 4% As) was skimmed off. If arsenic in the bullion remained above 0.3%, the excess was extracted into caustic soda. The bullion was then ready for Betts electrolytic refining (p 245).

Drosses were subsequently processed in a reverberatory dross retreatment furnace to produce a matte-speiss mixture for sale to a copper smelter, or for production of copper sulfate at Trail (p 245). CM&S consumed copper sulfate as a flotation reagent at the Sullivan concentrator, and also for solution purification in the zinc oxide leaching plant. Residual slag from copper dross retreatment was stored for recovery of lead, tin, and indium (p 246).

C. Blast Furnace Slag Fuming

<u>Fuming</u> of BF slag consumed about 200 lb of dried coal per minute (55 tons of BF slag fumed for 160 minutes). Fumed slag (2.3% Zn, 0.09% Pb, 33% Fe, 29% SiO₂, 12% CaO, and 8.5% Al₂O₃) was granulated, then went to waste. The leady zinc oxide dust (for processing in the zinc plant) was carried by the hot exhaust gas through a boiler for heat recovery, through a water-spray cooling flue, and then into a baghouse. The cleaned gas was vented to a stack (p 243; pp 246-248).

D. The Lead Refinery

- <u>Lead refinery</u> capacity in 1954 was 600 stpd (p 250). This refinery converted drossed BF bullion via Betts electrolysis to pig lead (99.99% Pb). The principal byproduct of electrolysis was slimes containing the Ag, Au, Bi, Cu, and Pb. The main outlet for antimony and arsenic was through the silver refinery (p 275). Outputs shown in the simplified flow diagram on p 250 are dross (to the smelter) and Sb-As-Sn slag (to antimonial lead production).
- About 3.5 lb of the <u>tankhouse electrolyte</u> per pound of refined lead exited from the tankhouse. Electrolyte contained 85 gpl Pb and 95 gpl H₂SiF₆. Losses were made up by addition of a 25% solution of H₂SiF₆ acid. Electrolyte volume was

depleted when cathodes were removed from the tanks, by evaporation, and due to other unspecified losses (p 256).

E. The Silver Refinery

 <u>The silver refinery</u> processed Trail Betts refinery slimes. Principal outputs were silver and gold bars. Byproduct liquids and solids contained substantial values. These streams were therefore either sent back to the smelter for additional processing, or were sold. An exception was copper nitrate liquid effluent generated when parting silver from gold. See Figure A1 for details (p 257).



Figure A1. The silver refinery

Most of the copper had already been recovered by cupellation prior to parting. The volume of copper nitrate liquid waste was likely not large, in that it was a product of the silver refinery. The Betts slimes feedstock to the refinery (13 dry tons per day) assayed about 1.8% Cu, 11.5% Ag, 0.016% Au, 38% Sb and 11% As. Metal yield after melting was 40 to 50% (pp 254, 257, 260).

<u>Antimony, arsenic, and bismuth:</u> Antimony and arsenic were rejected by volatilization during slime melting and subsequent *burning down* (fuming) using air blowing. These fumes were cooled indirectly in tubes, then passed though a baghouse to recover the condensed dust. This Sb- and As-rich dust was either processed to recover antimony, or sold.

The burned down (fumed) metal was then further oxidized (by *cupellation*) to produce about 1,500 lb/day silver-gold dore metal. Bismuth (Bi), Pb, Cu, and residual precious-metal values were subsequently recovered from the dore-furnace slag in the bismuth refinery. See Table A3 for chemical analyses.

•		()	Percentag	ges)				
PRODUCTS	Au	Ag	Pb	Sb	As	Cu	Bi	Sn.
Slime		11.5	19.7	38.1	10.6	1.8	2.1	0.07
Slime Melting Slag		0.07	26.9	36.3	3.8	0.13	0.05	0.30
Slime Melting Metal	0.02	20.1	23,0	35.2	8.1	6.5	3.5	
Burned Down Metal	0.04	33.9	34.0	12.0	1.4	10.8	6.1	
High Antimony Dusts	30,0004	0.05	3.2	53.7	14.1	0.06	0,10	0.08
Doré Metal	0.13	99.3	0.03			0.5		
Cupellation Slag	<u> </u>		42.8	13.2		5.8	13.9	
High Silver Dusts	0.0003	0.6	21.4	30.8	6.9	0.15	1.6	0.05
Litharge Metal	0.001	4.6	65-70				23-27	
Litharge Reduction	•						-0 2.	
Slag	0.0001	0.2	36.5	20.7	2.7	1.4	0.9	_
Copper Speiss	0.007	7.7	9.1	21.9	4.4	46.5	2.1	
Desilverized Lead-				-1.0		-0.0		6
Bismuth Metal		0.0001	7075			< 0.0001	25-30	57 G <u>149</u>
Fine Silver			< 0.002		—		< 0.001	
Gold	95.1	3.3						
*Guaranteed Minin								

 Table A3: Typical Analyses of Silver Refinery Products

(Anonymous, 1954, p 260)

Production of bismuth at Trail began in 1929. Byproducts produced during recovery of bismuth, which tended to contain significant metal values, were recycled within the Trail smelting and refining complex.

F. Antimony Production

 <u>Production of antimony</u> at Trail began in 1938. The antimonial lead plant processed high-Sb dusts from the silver refinery, dross produced from Betts cathodes, and slag from the lead refinery dross retreatment furnace. Principal outputs were Pb-Sb alloy products, baghouse dust to stock, and dearsenizing slag to waste. See Figure A2 and Table A4. (p 260-261).

The Sb-rich feedstocks were processed in a reduction furnace at about 1800 F with coal, including caustic soda as a flux. Outputs were Pb-Sb-As bullion, dearsenizing slag, and high-As dust. The dust assayed 34.2% As, *which is collected in a baghouse for disposal* (pp 260 - 261).



Figure A2. The antimonial lead plant.

Table A4:	Average Analyses of Materials from the Antimonial Lead Plant
	(Anonymous, 1954, p 261)

	Ag (oz./ton)	Cu %	Fb %	Sb %	As %	$\overset{\mathrm{Bi}}{\%}$	Sn %
Silver Refinery Baghouse Dust							<0,05
Reduction Metal	<u> </u>	0.05	5.82	35.4	5.5	0.11	
Antimonial Lead	8.0	0.04	74.6	25.0	0.02	0.08	
Antimonial Lead Baghouse Dust.			2.3	31.0	34.2		
Dearsenizing Slag (Typical)		-	23.0	7.0	17.0		

The bullion was dearsenized in a kettle with caustic soda and fine lead dross, producing sodium arsenate. This dearsenizing slag (17% As) was returned to the reduction furnace for Sb-Pb recovery.

G. The Zinc Department

 <u>The zinc department</u> began production in 1916, and by 1954 its capacity was 560 tons/day of cathode. About 320,000 tons of zinc concentrates were processed annually. An additional 75,000 tpy of zinc oxide fume was processed. This additional zinc originated from lead concentrate, some crude ores, and zinc leaching residue. Cadmium output was 2,000 lb/day (pp 262-263).

Heat from zinc concentrate roaster gas (6 to 7% SO₂) was recovered by boilers. Preliminary dust collection (20%) occurred in the boilers. Cycloning the boiler exit gas brought total dust recovery to over 90%. The recovered dust was returned to the suspension roasters. Next came electrostatic precipitators, the dust from which went directly to leaching (p 266).

- <u>Handling roaster gas</u>: Final roaster gas cleaning prior to SO₂ recovery entailed scrubbing with water saturated with SO₂. Collected solids were settled from the recirculating scrubber water. Aqueous purge from the recirculating water went to waste. The scrubbed gas then was rescrubbed and passed though Cottrells to reject all but 1% of the dust, as well as acid mist (p 266; pp 290-291). The coarser scrubber solids settled out in Glover Pond, through which scrubber water flowed prior to discharge to the Columbia (B.C. MoE Phase 1 Study, 1977, p 119).
- <u>Calcine and fume leach residue</u>: Roasted calcine and fumed zinc oxide were leached separately with spent electrolyte and make-up sulfuric acid to generate zinc sulfate for electrolytic production of zinc. The calcine leach residue, which usually returned to the lead smelter, on average assayed 25.7% Fe, 21.4% Zn, 11.9% Pb, 7.2% S, 3.6% SiO₂, 1.7% CaO, and 0.55% Cd (p 269). See Table A5 for the assay of the residue from leaching the fumed zinc (p 276).
- <u>Tankhouse electrolyte purge</u>: Leach liquor purge from both the calcine and fume leaching sections was electrolytically stripped down to 10 to 15 gpl Zn, then converted to a zinc-ammonium-sulfate complex for sale as micronutrient (p 278). This purge was essential to purge soluble impurities, including chloride, fluoride, and magnesium.

	(Anonymous, 1954, p 276)								
•	Pb [:] %	Zn %	Total SS %		SiC ₂ %	Fe %	Cd %	Ge %	Cl %
Fume from baghouse Fume from flues Plant residue	$11.5 \\ 17.7 \\ 37.6$	$65.1 \\ 55.7 \\ 7.8$	1.6 2.5 9.1	$1.2 \\ 2.0 \\ 7.9$.3 1.3 3.5	.3 .6 8.3	.38 .60 .28	.023 .021 .038	.04 .05

Table A5: Fume Plant Feed and Leach Residue

H. Cadmium Recovery

- <u>The cadmium plant</u> applied leaching and electrowinning to recover cadmium from the various Cd-rich plant byproduct streams. Sullivan zinc concentrate averaged about 0.14% Cd. Other concentrates fed to Trail averaged about 0.36% Cd.
- <u>Cadmium sponge</u>: Other than cathode zinc and electrolyte purge, the principal other outfall from the zinc plant was the cadmium sponge derived from purification of the zinc sulfate leach liquor, prior to zinc electrowinning. This byproduct went to the cadmium plant (p 268; p 274).
- It was occasionally economic to leach <u>BF baghouse dust</u> for recovery of its cadmium values. The BF baghouse dust averaged about 3% Cd, a portion of which was present as sulfide. Cadmium extraction by leaching averaged 90%. Alternatively, the Cd-rich BF dust could be blown into the exit gas from slag fuming. Sulfides were oxidized; Cd then reported to the fume leaching circuit (p 275).

About 50% of the Cd entering zinc calcine and fume leaching was dissolved, then precipitated as Cd sponge via addition of zinc powder. The balance (about 50%) returned to the lead smelter, where the Cd (very volatile) concentrated in the BF baghouse dust. This dust returned to the sintering plant, building up a circulating load of Cd. When this load became sufficiently high, this Cd-rich dust could be processed along with the dust produced during slag fuming (p 280).

- During <u>electrowinning of Cd</u>, impurities built up in the electrolyte (primarily F, Ca, Mg, Tl, Ni). A portion of the electrolyte (150 gpl Cd and 61 gpl Zn) was therefore purged to removed these impurities from the tankhouse. This purge was returned to the fume leach circuit.
- <u>Thallium (TI)</u> was rejected from the cadmium plant using permanganate, which oxidized the thallium to the relatively insoluble thallic form. This precipitate ultimately returned to the lead smelter via addition to the zinc fume leach residue.

APPENDIX B: GLOSSARY OF TERMS

Ag: Silver

AI: Aluminum. Alumina (Al₂O₃) is a component of slag.

Anode: Lead at Trail was cast into flat shapes called *anodes* prior to subjecting them to electrorefining to produce purified cathodes. Impurities collected as slimes, which were processed in Trail's precious-metal refinery.

As: Arsenic

Ash: Ash is impurity mineral matter in coal or coke. During smelting, ash becomes a component of the slag.

Au: Gold

Baghouse: A baghouse captures dust by passing the gas through supported cloth socks. The dust is periodically released from the socks either by shaking, or with a puff of air. Baghouses typically collect dust more efficiently than do Cottrells.

Bi: Bismuth

Blast furnace (BF): A vertical smelting furnace that Trail used to recover lead, copper, and byproduct metals from ores and concentrates.

Blast Roasting: Agglomeration of particulate solids by roasting, prior to BF smelting of these solids.

Briquetting: Pressing of particulates into pillow-shaped agglomerates prior to BF smelting.

Cathode: The metal product from an electrolytic process. At Trail, lead cathodes were produced by Betts electrorefining, and zinc cathodes by zinc electrowinning.

Cd: Cadmium, which is a reasonably volatile element.

Coke: Coal that has been heated to remove volatile constituents. Coke is an important part of the charge fed to a BF.

Concentrate: Trail's two primary feedstocks were zinc and lead concentrates. Ore was upgraded to reject waste minerals (gangue), thus concentrating the zinc sulfide (ZnS) and lead sulfide (PbS) mineral values.

Cottrell: Gas carrying entrained dust is ionized in a Cottrell. Dust particles in this media gather sufficient electric charge to move under the force of the electric field, and thus are collected. These devices are also called electrostatic precipitators (ESP).

Cu: Copper, a non-volatile metal that is easily recovered by smelting.

Cyclone: A cone-shaped device in which gas containing dust is spun in a manner that separates out the coarser solids.

Dross: A solid or semi-solid residue that forms on top of molten metal, e.g., when refining impure lead in iron kettles. The dross is skimmed off.

Electrorefining: Refining a metal by using electricity to dissolve it (from an anode), followed by deposition of the metal from solution (on a cathode). Trail recovers lead by Betts electrorefining. Betts, a Trail technologist, invented the process.

Electrowinning: Recovering a metal by using electricity to deposit the metal directly from solution as a cathode. Trail recovers zinc by electrorefining this metal from purified zinc sulfate solution. This solution was made by leaching zinc oxide calcine. The calcine was produced by roasting zinc sulfide concentrate.

ETP: Effluent Treatment Plant, which precipitated metals via lime neutralization from Trail's waste liquor prior to its discharge to the river.

Fe: Iron. Iron oxide (Fe₂O₃) is an important component of slag.

Flue: A tube, pipe, or shaft designed to transport hot gas.

Flux: Additives to a smelting operation that combine with gangue minerals to produce slag having suitable physical and chemical properties.

Fume: Fume is gas that contains volatilized metal. One can also *fume* a slag in order to boil off a portion of metals contained in the slag. Scrubbing is an efficient means to recover metals from the evolved fume.

Gangue: Worthless minerals associated with economically valuable minerals. Gangue minerals are a major component of slag.

Granulation: Molten slag is granulated by spraying it with high-pressure water.

Halides: Chlorides and fluorides, which are impurities that interfere with economic electrowinning of zinc. These halides were rejected at Trail by leaching fumed zinc oxide with soda ash solution.

Hg: Mercury

Leaching: Solids particulates are mixed with an aqueous solution to dissolve at least a portion of the feedstock. Thickening and/or filtration follows.

Lime: Calcium oxide, which is often used to neutralize acidic waste solutions.

Limestone: Calcium carbonate rock, which is often used as a flux to improve slag physics and chemistry.

Matte: A dense mixture of metallic sulfides that is often a product of smelting and refining.

Norzink Process: This process Trail used as a final mercury removal step from flue gas just prior to converting sulfur dioxide in the gas to sulfuric acid.

O: Oxygen

Ore: A naturally occurring collection of minerals that can be economically processed to recover metal values.

Pb: Lead

Purge: Impurities can build up in a solution during processing, e.g., in the electrolytes used during electrolysis of lead and zinc. A portion of the contaminated electrolyte is therefore removed (*purged*). Purged liquor is replaced by fresh pure electrolyte. Whether purged liquor is discarded or processed for reuse depends on technical, economic, and environmental constraints.

Refining: Processing of impure metal-rich intermediates to remove impurities.

Reverberatory Furnace (RVF): A horizontal smelting furnace, used by Trail in the early years to smelt copper ores.

Roasting: Combusting solid substances to drive off a volatile component, such as sulfur as sulfur dioxide. At Trail, ZnS concentrates were roasted to produce ZnO and sulfur dioxide gas (SO₂).

S: Sulfur. When sulfur combines with lead, zinc, or copper, the resulting compound is a sulfide, e.g., PbS.

Sb: Antimony

Scrubbing: Scrubbing involves contacting a flue gas with an aqueous solution, often as a fine spray, to capture dust entrained in the gas. Scrubbing also cools the gas,

primarily by evaporation. During scrubbing, much of the metallic fume carried in the gas is condensed and recovered, e.g., arsenic, cadmium, and mercury.

Si: Silicon. Silica is SiO₂, which is a common gangue component.

Sintering: Heating fine solids to produce semi-fused porous chunks, in preparation for blast-furnace smelting. Trail operated Dwight-Lloyd (D&L) continuous sintering machines.

Skulls: Frozen residual metal that freezes on the ladle after the bulk of the metal has been poured off.

Slag: A byproduct of high-temperature recovery of metals. In the context of this report, slag is a glass-like material consisting primarily of silica, lime and iron oxide, as well as small amounts of base metals, including zinc, lead, copper, arsenic, and cadmium.

Slimes: Precious-metal-rich particulates that remain behind when electrorefining metallics. Slimes are sent to a precious metal refinery to recover values, e.g., gold and silver.

Smelting: Melting, and then processing metal-containing feedstocks to separate out valuable components. Inert oxides float upwards as slag; the metallics and matte sink, to be collected separately by tapping the furnace.

Soda Ash: A basic solution of sodium carbonate that Trail used to leach halides away from fumed zinc oxide.

Speiss: A mixture of metallic arsenides produced during smelting. A common component of speiss is iron arsenide, which is an alloy of arsenic and iron.

Stripping Cells: In stripping cells, electrolyte purged from the zinc tankhouse was processed at high current density to recover much of its zinc content. The stripped electrolyte output contained 13 to 18 gpl Zn.

Sulfide: Examples of sulfide are PbS and ZnS. Trail's lead concentrate contained PbS, i.e., a compound composed of lead and sulfide-sulfur. The zinc concentrate also was rich in sulfide, primarily ZnS.

Sulfuric Acid: This acid (H_2SO_4) is produced by combining SO_2 gas with moisture and oxygen in the presence of a catalyst. The flue gas must first be thoroughly scrubbed to remove dust and fume, which would otherwise poison the catalyst.

Tankhouse: A building in which electrolytic processing of metals takes place in tanks.

Tapping: One taps a furnace through an opening to permit metal, slag, matte, or some other molten component to discharge from the furnace.

Thickener: Solids suspended in aqueous solution, e.g., precipitate formed by neutralizing waste solution in Trail's Effluent Treatment Plant (ETP), can be allowed to settle, then recovered. The device in which the solids are settled is called a *thickener*.

Zinc Dust: Fine zinc metal powder that is mixed with zinc sulfate solution to precipitate impurities.

Zn: Zinc, which arrived at Trail primarily as ZnS, i.e., zinc sulfide.

APPENDIX C: REFERENCES CITED, REVIEWED, AND CONSIDERED WHILE PREPARING MY EXPERT OPINION, INCLUDING TECHNICAL PAPERS, BOOKS, AND DOCUMENTS (Separate File)

APPENDIX D: INPUTS AND DISTRIBUTIONS SPREADSHEETS, AND EXPLANATION OF SPREADSHEET DETAILS (Separate File)

APPENDIX E: PAUL B. QUENEAU – C.V.

Paul B. Queneau P.B. Queneau & Associates, Inc. The Bear Group Golden, CO 80403

Phone: (303) 854-2036; Fax: (303) 273-0494

Areas of Expertise

Extractive metallurgy, metals recycling, resource location, and byproduct marketing.

Experience Summary

Dr. Queneau's technical and project management responsibilities focus on extractive metallurgy of nonferrous metals, treatment of metal-containing wastes, resource location and byproduct marketing. His 43 years of experience include the

development of custom processes for primary and secondary feedstocks, plant startups and plant operation to increase output, yield, and product quality.

In-plant projects include recycling of tin solder and drosses, Ni-Co recovery from laterite ore (pressure acid leaching, Australia), processing spent copper etchants (Hong Kong), processing and utilization of nonferrous and waste-processing slags, production of ferro-niobium from enriched slag (Brazil), conversion of tungsten concentrates (U.S. and Russia), processing tantalum intermediates, production of molybdenum chemicals, Ni–Mo-W recovery from spent catalyst (Europe), recycling copper flue dust, production of secondary bronze ingot, recycling leady residues (seven plants in U.S., Canada, and Mexico), processing hazardous waste in rotary kilns (seven plants), production of antimony oxide (Bolivia), producing zinc and manganese micronutrient (five plants), recycling of secondary aluminum in short rotary furnaces (four plants), silver production (U.S. and Turkey), production of defluorinated phosphate, recycling calcium fluoride, processing ferromanganese furnace dust, and Ni-Cu-Co recovery from matte.

As an R&D supervisor for AMAX in Golden, CO, Paul Queneau led research on production of ammonium paratungstate (APT), leading to commercialization; he also led the team that innovated AMAX's acid pressure leach for treating nickeliferous laterite. Dr. Queneau was a member of the AMAX process engineering team that started up atmospheric and pressure leaching circuits, residue flotation and hydrogen reduction plant at Port Nickel. As a research engineer at Kennecott, he developed the process, then supervised the startup of a five-ton-per-day plant to upgrade high-rhenium molybdenite inventory.

Credentials

Ph.D. Metallurgical Eng., U. of Minnesota, 1967. B.S. Metallurgical Eng., Cornell University, 1964.

Member of the American Institute of Mining, Metallurgical and Petroleum Engineers (AIME), Mining and Metallurgical Society of America, and Canadian Institute of Mining and Metallurgy (CIM).

AIME-TMS 2001 Extraction & Processing Distinguished Lecturer Award. Past President of the Denver Section, AIME-ASM Chapter.

Elected to membership in Tau Beta Pi Adjunct Professor at the Colorado School of Mines (CSM).

Registered Professional Engineer, Colorado; Authored 33 technical papers; holds 30 U.S. patents.

Employment History

1997 – Present	Consulting Metallurgical Engineer
	P.B. Queneau & Associates, Inc.,
	The Bear Group
1990 – Present	Adjunct Professor
	Colorado School of Mines
1983 - 1997	Principal Metallurgical Engineer
	Hazen Research, Inc.
1982 - 1983	President/Owner
	P. B. Queneau Company, Inc.
1972 - 1982	R&D Supervisor
	AMAX, Inc.
1967 - 1972	Research Engineer
	Kennecott Copper Corporation

Key Projects

Developed and proved process to produce tungsten chemicals from scheelite and wolframite concentrates. A profitable commercial operation resulted.

Established operating criteria and started up plant to produce antimony oxide at a tin operation in Bolivia; a profitable operating facility resulted.

Worked with venture capital firms to evaluate the current capabilities and future potential of U.S. zinc smelters.

Evaluated primary zinc plant (roast/leach/electrowin) as an acquisition candidate for processing sphalerite concentrate output from proposed mine/concentrator.

Worked with slagging kiln incineration operations to maximize throughput, and with ingot-plant and industrial waste furnaces to enhance slag quality and marketability.

Doubled the lead output from a Canadian secondary lead producer over a two-year period by implementing a computer model to optimize feedstock selection and blending, and coke-flux inputs.

Worked closely with waste management operation in Hong Kong to recover copper from spent etchants and to market byproduct salts produced.

Assisted lead-acid battery recycler with selection of blast furnace formulations to maximize slag environmental acceptability without significantly affecting production efficiency.

Detailed technologies for nickel and cobalt recovery from spent lithium ion, nickel metal hydride, and NiCd batteries. Worked out N. American sources of these spent batteries, as well as capabilities of the established recycling operations.

Provided in-plant technical support to produce bronze secondary ingot from red-metal scrap, increasing the quality and quantity of alloy output.

Upgraded operating practices of rotary furnaces converting complex tin drosses to solder, improving yield by over 20%.

Carried out an in-depth technical and marketing evaluation for producing byproduct MnSO₄ and MnO, resulting in a profitable production facility.

Provided onsite startup assistance (three months) for large silver production facility in Turkey.

Worked with an international oil firm to evaluate alternative outlets worldwide for recycling spent resid and HDS catalyst.

Improved Al[°] furnace yield while recovering NaCI-KCI-NaF and Al[°] fines from salt cake at U.S. secondary aluminum smelters. Worked out alternative markets for the metallic aluminum fines.

Provided technical support for facility manufacturing molybdenum chemicals: troubleshooting, unit operation startups and new product development.

Selected and evaluated three routes to recover Mo/Co/Ni chemicals and aluminumrich byproducts from spent catalyst; detailed market outlets.

Developed wet oxidation - solvent extraction process to recover vanadium and nickel from Venezuelan petroleum coke.

Identified volumes and producers of etchant, alternatives for processing the outputs, and market outlets for products therefrom.

Provided startup expertise to a refinery producing nickel, cobalt, and copper from matte; work included startup of the leaching and reduction operations.

Worked out handling of phosphorus electric furnace slags. Developed byproduct alternatives for the furnace flue dust.

Developed a process for beryllium hydroxide recovery from phenacite concentrate by leaching, solution purification, and precipitation.

Evaluated alternative technologies to recover gallium and germanium from carboniferous shale. Later examined likely areas worldwide for increased Ge output in response to escalating Ge price.

Worked with aircraft manufacturer to evaluate VC₄ production in U.S., Europe and Japan.

Worked with EPA contractor to assemble "a guide on recycling low-metal-content wastes for use by decision makers at superfund, RCRA, and other waste sites."

Presented on-site short courses on recycling metals from industrial waste. Locations include CSM, a DOE facility, EPA's Office of Solid Waste in Washington, AIME and CIM annual meetings, and at a waste processing facility.

Assisted in the startup of a rhenium-chemical production facility from roaster flue gas.

Helped chemical producer to identify opportunities for production of nickel and cobalt chemicals, as well as secondary sources for feedstocks.

Worked with team evaluating hydromet process for Ni, Cu, Au, and pgms, recovery from flotation concentrates.

Worked with firm producing chromated copper arsenate to establish secondary sources for its copper, chromium, and arsenic raw materials.

As Technical Assessor reporting to the Tribunal for an international arbitration related to nickel production, was responsible for documenting agreements between 28 expert witnesses and providing technical assistance to the Tribunal during the trial.

Books

Meeting Chairman and Editor, <u>Third International Symposium on Recycling Metals</u> and Engineered Materials, Point Clear, Alabama, The Metallurgical Society of AIME, Warrendale, PA (1995).

Editor, <u>International Symposium on Residues and Effluents Processing</u>, The Metallurgical Society of AIME, Warrendale, PA (1991).

Editor, <u>Symposium on Arsenic Metallurgy: Fundamentals and Applications</u>, The Metallurgical Society of AIME, Warrendale, PA (1987).

Technical Publications and Presentations

Recycling Metal-Rich Industrial Products, 375th Anniversary, Nickelhütte Aue, Aue, Germany (2010).

Rich Country – Rich Wastes: Meeting Needs and Grasping Opportunities, <u>MiMeR/Boliden Foresight Seminar</u>, Lulea, Sweden (2008).

Recent Developments: Specialty U.S. Metals Recycling Plants, <u>Recycling Metals from</u> <u>Industrial Waste Short Course</u>, Colorado School of Mines, Golden, CO (2008).

Recycling Zinc in the United States, <u>The El Digest Gathering</u>, San Diego, CA (September 2005).

Hazardous Waste to Valued Byproducts, <u>The El Digest Gathering</u>, San Diego, CA (September 2004).

Recycling Non-Ferrous Metals from Industrial Waste, <u>Hydrometallurgy 2003</u>, AIME/TMS, 1543 – 1553.

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Production of Copper Chemicals from Secondary and Byproduct Sources in the United States, <u>Journal of Metals</u>, 34-37, 49 (October, 1997).

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State of the Art in Mercury Recycling, <u>Intl. Symp. on Treatment and Minimization of</u> <u>Heavy-Metal Waste</u>, AIME/TMS Annual Meeting, Las Vegas (Feb. 1995).

Secondary Zinc Production and Waste Minimization, <u>Pollution Engineering</u>, 42-44 (November, 1994).

U.S. Mercury Recyclers Expand Process Capabilities, <u>Hazmat World</u>, 31-34 (February, 1994).

Recycling Lead and Zinc in the United States, <u>4th Intl. Symp. on Hydrometallurgy</u>, Salt Lake City (1993).

Waste Minimization: Recycling of Spent Lead-acid Batteries, <u>Hazmat World</u>, 34-37 (August, 1993).

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Application of Slag Technology to Recycling of Solid Wastes, <u>Intl. Incineration Conf.</u>, Knoxville (1991).

Optimizing Matte and Slag Composition in Rotary- Furnace Lead Smelting, <u>Intl. Symp.</u> on Primary and Secondary Lead Processing, 145-178, Halifax (1989).

Processing Petroleum Coke to Recover Vanadium and Nickel, <u>Hydrometallurgy</u>, vol. 22, 3-24 (1989).

Germanium Recovery at Lang Bay, <u>CIM Bulletin, 79(886)</u>, 92-97 (February, 1986).

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Control of Silica Deposition during Pressure Let-down of Acidic Leach Slurries, <u>Third</u> <u>International Symposium on Hydrometallurgy</u>, 121-137 (1983).

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Patents

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> Paul B. Queneau P.B. Queneau & Associates, Inc. The Bear Group Golden, CO 80403 Tel: (303) 854-2036

EXPERT OPINION OF PAUL B. QUENEAU PAKOOTAS, ET AL. v. TECK COMINCO METALS ET AL.

September 15, 2010

Jan Inenean

Paul B. Queneau