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July 1982

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AIR POLLUTION EMISSIONS AND CONTROL TECHNOLOGY: PRIMARY COPPER INDUSTRY

by

Mineral and Metal Processes Division
Engineering Assessment Branch
Air Pollution Control Directorate

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ABSTRACT

Current industrial technology in the primary copper producing industry with emphasis on smelting, is reviewed.

The processes used, and air pollution emissions and control technology with emphasis on sulphur fixation, are described.

The size and composition of the world-wide industry is reviewed. Canadian copper producing operations are described.

The cost of development and operation of primary copper production processes with emission controls is discussed.

RÉSUMÉ

Les techniques actuelles de l'industrie du cuivre de première fusion sont passées en revue, et une attention particulière est accordée aux procédés de fusion.

Les procédés employés sont décrits, ainsi que les émissions atmosphériques, les techniques antipollution, et notamment la fixation du soufre.

L'importance et la composition de l'industrie mondiale est examinée, et les installations canadiennes sont décrites.

Les coûts de mise au point et d'exploitation de procédés de production incorporant des dispositifs antipollution sont examinés.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 INTRODUCTION

This study of the copper industry was done as part of Environment Canada's non-ferrous acid precipitation program. This program is designed to develop a set of feasible SO_2 control strategies for the Eastern Canadian non-ferrous smelter sector as part of the overall program to abate or reduce acid precipitation. It is restricted to the copper-nickel sector of the non-ferrous industry since this sector emits the vast majority of the SO_2 from Canadian sources.

The study was written using the background document developed by the United Nation Economic Commission for Europe Non-Ferrous Task Force (1) as well as other published and in-house material.

1.1 General Description of the Primary Copper Industry

Primary copper-smelting is characterized by the use of copper ore as process material, which can be classified into sulphide, oxide, or sulphide-oxide ores. The type of ore will determine the process to be used for recovering copper. Part of the demand for copper can be met by processing copper scrap in secondary copper-smelting plants.

After mining, copper is recovered by beneficiation of the ores, followed by smelting or leaching, and subsequent refining.

Copper is present in the mined copper ores in a variety of compounds together with worthless gangue (e.g. silicates), ferrous sulphides, other utilizable metal sulphides (e.g. zinc, nickel, lead), and precious metals. Worldwide, the majority of copper ores are sulphides, although there are substantial quantities of oxide ores and lesser amounts of others.

Copper is mined in the provinces of Newfoundland, Quebec, Ontario, Manitoba, Saskatchewan, British Columbia and the Yukon Territory. The majority of copper mined in Canada is from sulphide ore bodies (one deposit in B.C. has some native copper and one in Gaspé, Que. some copper oxide) and often has nickel, zinc, molybdenum, gold, silver and other metals associated with it in recoverable concentrations. Some copper is recovered from zinc or nickel sulphide ore bodies. The Canadian copper industry, in general, is in the lower cost production category, largely because of the recoverable co-products and by-products.

Around 1965, the average copper content of ores being mined ranged between 1.5 and 2% compared to 20% in 1860. Today, the average copper content of the world copper ore production is about 1.0%; in Canada, it is 0.7%. Tables 1 and 2 show world copper reserves and mine production respectively.

The world copper ore production from open-cast mining has increased steadily during recent years compared with that from underground mining. In 1970, the share of open-cast mining was 55%, and in 1973, 85% of the copper ores were mined in open-cast mines (21).

The world's smelter production of copper has increased from 4 960 000 tonnes in 1967 to 8 130 000 tonnes in 1978. The average annual increase during this time is approximately 4%. Tables 3 and 4 show the world smelter production and refined production of copper respectively.

Table 5 shows Canada's international position with respect to copper. Canada has about 5% of the world's reserves and 10% of mine production. One third of the Canadian copper is exported in concentrate form, mostly from British Columbia. Canada is a net exporter of copper metal as well.

TABLE 1 WORLD COPPER RESERVES, BY CATEGORY AND AVERAGE GRADE AS OF 1977 (67)

	I. Producing mines[b]		II. Under construction		III. Other known deposits		Total (I + II + III)	
	Copper content (thousand tonnes)	Average grade (%)	Copper content (thousand tonnes)	Average grade (%)	Copper content (thousand tonnes)	Average grade (%)	Copper content (thousand tonnes)	Average grade (%)
Canada	16 500	0.70	500	1.21	7 400	0.48	24 400	0.62
United States	60 400	0.71	6 300	1.21	13 400	0.63	80 100	0.71
Mexico	11 700	0.60	5 900	0.75	5 800	0.72	23 400	0.67
Panama	-	-	-	-	12 000	0.60	12 000	0.60
Others	800	0.8	-	-	2 300	0.75	3 100	0.76
North and Central America	89 400	0.69	12 700	0.94	40 900	0.60	143 000	0.68
Peru	9 400	1.07	6 800	0.68	11 100	0.88	27 300	0.93
Chile[c]	58 500	1.11	3 300	1.70	18 000	0.84	79 800	1.07
Argentina	-	-	-	-	4 200	0.59	4 200	0.59
Others	-	-	-	-	1 900	1.10	1 900	1.10
South America	67 900	1.10	10 100	0.85	35 200	0.82	113 200	0.99
Zaire	30 900	3.90	4 300	5.02	6 400	4.1	41 600	4.05
Zambia	26 500	3.06	800	2.22	-	-	27 300	3.02
South Africa	4 000	0.71	1 000	0.8	-	-	5 000	0.73
Others	2 900	1.8	-	-	-	-	2 900	1.8
Africa	64 300	2.70	6 100	2.47	6 400	4.1	76 800	2.80
Philippines	9 400	0.54	3 200	0.44	3 300	0.46	15 900	0.50
Papua New Guinea	4 100	0.47	-	-	2 400	0.85	6 500	0.61
Australia	5 400	2.58	-	-	800	2.69	6 200	2.59
Iran	-	-	5 200	1.2	1 300	0.65	6 500	1.09
India[d]	2 300	1.4	-	-	2 300	1.3	4 600	1.35
Others	6 100	1.13	-	-	1 400	0.88	7 500	1.08
Asia	27 300	0.77	8 400	0.72	11 500	0.74	47 200	0.75

TABLE 1 WORLD COPPER RESERVES, BY CATEGORY AND AVERAGE GRADE AS OF 1977 (67) (cont'd)

	I. Producing mines[b]		II. Under construction		III. Other known deposits		Total (I + II + III)	
	Copper content (thousand tonnes)	Average grade (%)	Copper content (thousand tonnes)	Average grade (%)	Copper content (thousand tonnes)	Average grade (%)	Copper content (thousand tonnes)	Average grade (%)
Europe[e]	6 300	0.73	1 700	0.43	-	-	8 000	0.67
Centrally planned economy countries[fg]	36 700	1.57	16 300	1.72	10 000[d]	1.5[d]	63 000	1.60
World[h]	292 000	1.03	55 300	1.04	104 000	0.77	451 300	0.96

a Individual deposits with less than 100 000 tonnes copper content were generally not considered.

b As not all deposits in producing mines could be surveyed, a correction factor is included in the tonnage data. This factor is the ratio of the surveyed capacity to the total capacity of a country in 1976 and varies between 85 and 100 per cent; for the world, an average of 95 per cent of copper reserves in producing mines was surveyed.

c After compilation of this table, new official calculations became available which place proven and probable reserves about 10 per cent higher.

d Estimates.

e Excluding centrally planned economy countries, but including Yugoslavia.

f Estimates by Stolberg Ingenieurberatung GmbH, Stolberg, Federal Republic of Germany.

g Bulgaria, Hungary, Poland, Romania, U.S.S.R.

h Excluding China.

Source: United Nations Centre for Natural Resources, Energy and Transport.

TABLE 2 WORLD MINE PRODUCTION OF COPPER (TONNES)

	1975	1976	1977	1978	1979
United States	1 282 205	1 456 587	1 364 396	1 357 608	1 441 317
Canada	733 838	730 941	759 435	659 390	643 764
Mexico	78 200	88 996	89 722	87 181	104 418
Cuba	2 903	2 903	2 993	2 993	2 540
Nicaragua	635	798	299	99	99
Bolivia	6 168	5 080	3 719	3 265	1 723
Brazil	1 723	-	-	-	-
Chile	828 273	1 005 177	1 056 162	1 035 517	1 064 917
Peru	180 986	220 268	341 016	366 413	397 988
Total America	3 114 931	3 510 750	3 617 742	3 512 466	3 656 766
Austria	1 923	1 137	-	-	-
Finland	38 737	41 731	46 720	46 811	43 848
France	498	498	299	598	399
Germany, F.R.	1 961	1 613	1 210	820	816
Ireland	9 839	4 082	5 261	5 261	4 808
Italy	773	749	698	501	273
Norway	31 116	34 292	32 114	29 073	28 016
Portugal	2 063	1 760	1 431	1 369	2 099
Spain	56 881	50 803	53 252	46 539	41 840
Sweden	44 906	49 533	49 351	52 436	50 440
Total Europe	188 697	186 198	190 336	183 408	172 539
Cyprus	9 888	7 892	6 804	5 806	5 987
India	24 222	25 401	30 209	26 580	30 300
Indonesia	63 504	69 128	57 062	58 060	60 963
Iran	4 027	6 041	5 987	5 987	4 808
Israel	7 529	2 540	-	-	-
Japan	84 639	81 607	81 392	73 386	59 958
Republic of Korea	2 993	2 540	1 905	816	635
Malaysia	3 810	18 234	24 040	26 399	26 218
Philippines	248 935	262 452	300 736	290 304	297 047
Turkey	30 119	31 207	27 851	33 203	24 675
Total Asia	479 666	507 042	535 986	520 541	510 591
Botswana	6 531	12 337	11 702	14 605	12 972
Mauritania	6 622	9 434	7 711	2 812	-
Namibia	34 927	43 545	49 170	38 102	41 821
Republic of Zaire	494 786	444 437	481 632	423 843	400 347
Uganda	8 527	6 985	3 991	1 270	1 995
Republic of South Africa	178 927	196 881	205 390	209 291	194 412
Zambia	676 861	708 886	655 996	643 023	587 684
Zimbabwe	47 990	43 999	33 022	32 024	32 024
Total Africa	1 455 171	1 466 504	1 448 614	1 364 970	1 271 255
Australia	218 907	218 481	221 580	219 270	229 340
Papua New Guinea	172 479	176 520	182 293	198 606	170 825
Total Oceania	391 386	395 001	403 873	417 876	400 165
Sub Total	5 629 851	6 065 495	6 196 551	5 999 261	6 011 316
U.S.S.R.	1 099 980	1 130 008	1 099 980	1 139 987	1 139 987
Albania	8 981	9 979	9 979	11 521	11 975
Bulgaria	54 976	56 972	56 972	59 965	59 965
Czechoslovakia	10 704	8 527	9 344	9 979	9 979
Germany, D.R.	16 511	15 966	16 964	15 966	15 876
Hungary	362	272	181	90	-
Poland	229 975	266 988	289 306	317 973	319 969
Rumania	34 020	37 013	40 007	40 007	37 013
China and Other Asia (a)	155 040	165 019	170 009	178 990	175 996
Sub Total	1 610 549	1 690 744	1 692 742	1 774 478	1 770 760
Other Countries (b)	15 113	14 950	13 589	11 684	10 804
TOTAL	7 255 513	7 771 189	7 902 882	7 785 423	7 792 880

Source: American Bureau of Metal Statistics Inc., U.S. Bureau of Mines, World Bureau of Metal Statistics and various other sources

(a) Estimated

(b) Includes production in Algeria, Argentina, Burma, Congo (Brazzaville), Ecuador, Guatemala, Mongolia, Morocco, Mozambique and Taiwan.

TABLE 3 WORLD SMELTER PRODUCTION OF COPPER (TONNES)

	1975	1976	1977	1978	1979
United States	1 331 872	1 447 824	1 324 957	1 389 239	1 421 777
Canada	493 368	468 713	504 761	413 443	398 649
Mexico	61 508	85 186	87 544	87 000	93 532
Brazil	1 723	-	-	-	-
Chile	724 399	856 306	888 420	927 415	951 515
Peru	161 300	188 425	321 058	318 971	341 016
Total America	2 774 170	3 046 454	3 126 740	3 136 068	3 206 489
Austria	10 977	10 977	10 977	10 977	11 975
Belgium	40 007	72 031	61 598	55 883	56 972
Finland	46 176	50 258	60 782	62 868	55 883
France	2 812	2 177	5 261	3 175	4 989
Germany, F.R.	224 622	244 490	248 028	221 538	263 995
Norway	26 349	23 393	26 575	20 060	27 357
Portugal	3 175	2 903	3 265	2 993	3 265
Spain	104 963	112 492	117 482	112 492	114 035
Sweden	56 972	61 961	61 689	67 042	63 776
Yugoslavia	119 115	135 082	117 028	143 791	130 001
Total Europe	635 168	715 764	712 685	700 819	732 248
India	22 044	24 766	23 496	19 504	24 040
Iran	3 991	3 991	6 985	5 987	5 987
Japan	821 469	838 162	915 183	910 465	921 443
Republic of Korea	21 863	30 935	36 832	54 885	38 918
Taiwan	8 527	11 702	11 521	12 972	14 333
Turkey	27 034	28 123	31 298	26 218	22 407
Total Asia	904 928	937 679	1 025 315	1 030 031	1 027 128
Namibia	36 410	36 111	53 434	45 904	42 729
Republic of South Africa	166 834	168 013	188 425	189 423	176 541
Uganda	8 255	6 985	3 991	1 270	1 632
Republic of Zaire	462 581	412 957	442 985	390 731	370 046
Zambia	658 990	705 892	650 462	654 692	584 677
Zimbabwe	30 028	23 496	28 032	28 032	26 036
Total Africa	1 363 098	1 353 454	1 367 329	1 310 052	1 201 661
Australia	182 619	170 372	171 370	167 832	170 825
Sub Total	5 859 983	6 223 723	6 403 439	6 344 802	6 338 351
U.S.S.R.	1 099 980	1 143 979	1 099 980	1 170 015	1 170 832
Albania	8 527	8 981	8 981	9 525	9 434
Bulgaria	59 965	56 972	56 972	59 965	59 965
Czechoslovakia	9 979	9 979	9 979	9 979	9 888
Germany, D.R.	16 511	15 966	17 962	16 964	17 236
Hungary	2 540	5 171	3 810	-	-
Poland	229 975	269 982	290 031	319 969	320 060
Rumania	40 007	42 366	41 368	43 999	44 089
China and Other Asia (a)	177 992	184 978	194 957	194 957	194 594
Sub Total	1 645 476	1 738 374	1 724 040	1 825 373	1 826 098
TOTAL	7 505 459	7 962 097	8 127 479	8 170 175	8 164 449

Source: American Bureau of Metal Statistics Inc., U.S. Bureau of Mines, World Bureau of Metal Statistics and various other sources

(a) Estimated.

TABLE 4 WORLD REFINED PRODUCTION OF COPPER (TONNES)

	1975	1976	1977	1978	1979
United States	1 610 189	1 715 061	1 677 049	1 906 390	2 060 341
Canada	529 169	510 481	508 848	446 342	397 262
Mexico	69 763	75 388	79 017	83 008	100 517
Brazil	28 758	31 116	28 576	25 855	34 020
Chile	535 248	632 046	676 045	749 075	764 225
Peru	54 432	135 626	188 062	186 157	228 977
Total America	2 827 559	3 099 718	3 157 597	3 396 827	3 585 342
Austria	26 943	30 935	34 655	31 933	32 840
Belgium	331 581	425 023	464 667	388 644	378 483
Finland	35 834	38 193	42 819	42 729	43 001
France	39 644	39 191	44 997	41 277	45 360
Germany, F.R.	422 210	446 614	440 173	404 520	375 762
Italy	22 226	26 762	19 958	17 508	17 962
Norway	19 686	16 783	21 228	14 515	20 865
Portugal	3 175	2 903	3 265	2 993	3 265
Spain	130 183	141 886	160 030	146 966	144 335
Sweden	56 700	64 864	61 689	64 411	61 689
United Kingdom	151 502	137 168	122 199	125 556	121 655
Yugoslavia	137 894	136 533	143 519	150 776	138 438
Total Europe	1 377 578	1 506 855	1 559 199	1 431 828	1 383 655
India	13 245	21 228	22 770	11 702	30 300
Iran	6 985	6 985	6 985	5 987	5 987
Japan	818 929	864 380	933 690	959 091	983 676
Republic of Korea	21 863	30 935	42 910	62 415	59 875
Taiwan	7 076	11 702	11 521	14 515	14 333
Turkey	25 220	28 032	31 661	15 966	22 135
Total Asia	893 318	963 262	1 049 537	1 069 676	1 116 306
Egypt	1 995	1 995	1 995	1 995	1 905
Republic of South Africa	87 907	95 618	145 877	152 500	138 801
Republic of Zaire	225 892	66 044	98 703	102 785	102 876
Zambia	629 233	694 915	649 010	621 069	572 533
Zimbabwe	27 034	23 496	28 213	26 218	27 488
Total Africa	972 061	882 068	923 798	904 567	843 603
Australia	191 963	188 788	184 705	174 545	172 640
Sub Total	6 262 479	6 640 691	6 874 836	6 977 443	7 101 546
Albania (a)	5 987	6 985	6 985	6 985	7 257
Bulgaria	51 982	54 976	57 970	61 961	62 143
Czechoslovakia	22 770	22 135	23 133	24 040	24 040
Germany, D.R. (a)	46 992	29 986	50 984	48 988	49 260
Hungary	11 521	10 614	12 065	13 063	16 238
Poland	248 572	270 073	306 633	332 035	333 396
Rumania	44 997	44 997	46 992	47 990	47 990
U.S.S.R. (a)	1 399 991	1 420 040	1 439 998	1 480 006	1 479 915
China and Other Asia (a)	248 028	264 993	285 042	295 021	300 011
Sub Total	2 080 840	2 124 799	2 229 802	2 310 089	2 320 250
TOTAL	8 343 319	8 765 490	9 104 381	9 287 532	9 421 796

Source: World Bureau of Metal Statistics
(a) Estimated.

TABLE 5 CANADA-COPPER, 1977*

	World (000 tonnes copper)	Canada (000 tonnes copper)	Canada (as % of world)
Reserves	451,200	24,400	5.4
Mine production	8,028	759	9.5
Smelter production	8,125	504	6.2
Refinery production	9,102	509	5.6
Consumption	9,043	219	2.4

*1977 is the most recent typical year for which data is available. 1978 and 1979 data are unusual due to a nine-month labour strike at Inco Metals Ltd.

2 PRODUCTION PROCESSES

2.1 Processing of Copper Ores

The concentration of copper in most ores is too low for direct processing (smelting, refining); therefore, the ores must be beneficiated. In order to avoid transportation of worthless gangue, beneficiation is usually carried out at the mining site.

Beneficiation of copper ores is carried out mainly by flotation. Flotation requires comminution of the ores in order to separate the grains of copper minerals from the grains of the other minerals. Figure 1 shows the essential steps in concentrating copper ores. Crushing of large pieces of ore to a particle size of 10 to 20 mm takes place in jaw and cone crushers. Rod and ball mills are used for further grinding.

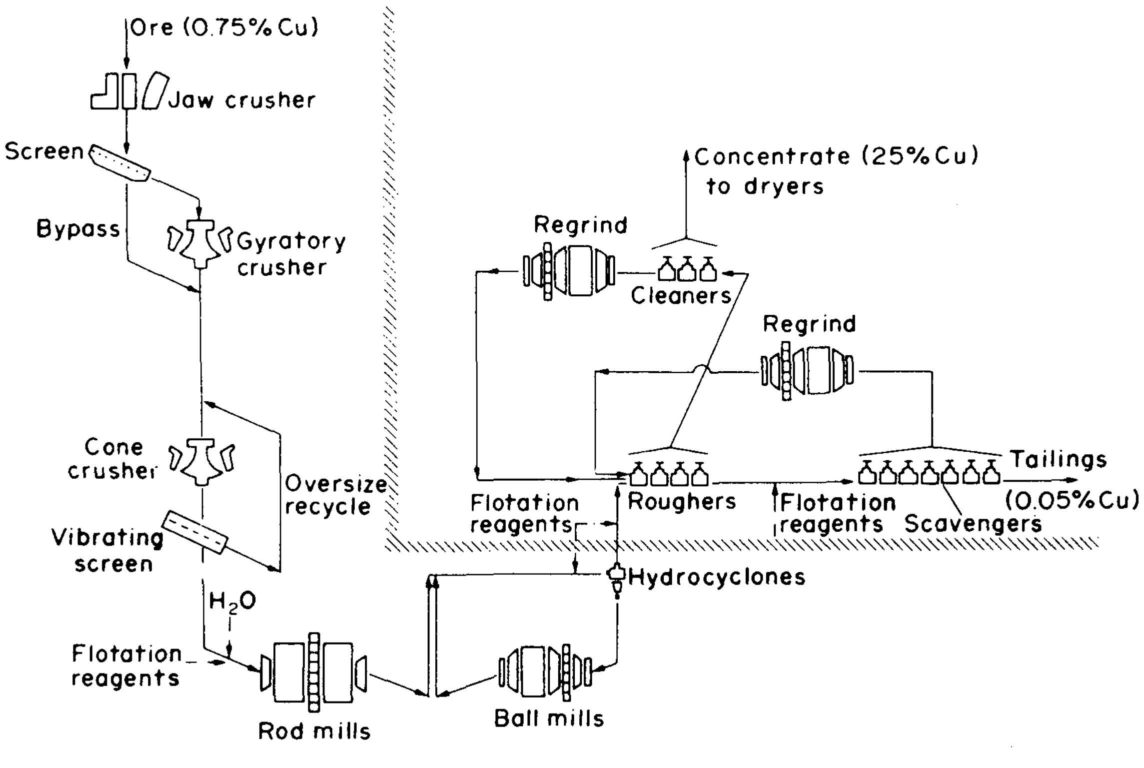


FIGURE 1 GENERALIZED FLOW SHEET FOR THE PRODUCTION OF COPPER CONCENTRATE FROM COPPER SULPHIDE-IRON SULPHIDE ORES. THE COMMINUTION AND FLOTATION SEQUENCES ARE SEPARATED BY THE SHADED LINE (3)

One method of beneficiating sulphide-oxide ores is the LPF (leach-precipitation-flotation) process, a combination of leaching and flotation. The ores are leached with sulphuric acid, the solution is cemented, followed by the separate flotation of the cemented copper and sulphide minerals in the leaching residue. Detailed information about flotation techniques for concentrating copper ores can be derived from specialized literature (3, 6).

2.2 Production of Copper

Extraction of copper from copper ores is carried out either by pyrometallurgical or hydrometallurgical methods. The use of either process will be determined by the conditions and circumstances for the operation of each copper extraction plant.

Sulphide copper ore concentrates and the richer oxidic copper ores are treated primarily by pyrometallurgical processes. Hydrometallurgical techniques for extracting copper are applied mainly to low-grade oxidic copper ores, sulphide-oxide ores, and some complex ores.

Advantages of the hydrometallurgical processes are:

- reduction of air pollution;
- treatment of ores which are lean in copper;
- economic mining of some smaller deposits;
- recovery of copper and other metals from some complex ores.

Advantages of the pyrometallurgical processes are:

- fast reaction;
- more effective extraction of precious metals (usually);
- treatment of chalcopyrite which occurs in large quantities and for which existing hydrometallurgical processes are not suitable;
- greater purity of copper produced by electrolytic refining compared with copper recovered by electrowinning;
- less energy intensive;
- fewer expensive reagents are required;
- greater economy of scale is possible.

2.2.1 Pyrometallurgical Processes. The pyrometallurgical processes consist of a varying number of steps up to the recovery of copper. The conventional technique consists of roasting, smelting, and converting.

The important processes are outlined in principle below. A distinction is made between the so-called conventional processes in which the various stages are carried out individually, and newer processes during the course of which some or all steps are integrated.

2.2.1.1 Conventional processes. The most common process employed in the approximately 80 copper smelters of the Western world is the technique of matte smelting which has been used for more than 100 years.

Copper matte is a copper-iron sulphide. It is composed of copper, sulphur, iron, and gangue and is extracted from sulphide ore concentrate. The conventional extraction process consists of the following steps which are carried out individually:

- roasting, i.e. removal of sulphur by introduction of air and simultaneous drying and heating of the concentrate to achieve a sulphur content favourable for matte smelting. (In cases where the concentrate already has a suitable sulphur content, this step may not be applicable);
- smelting, i.e. removal of part of the gangue for production of copper matte;
- converting to blister copper, i.e. removal of iron and the balance of the gangue by oxidation and slag-formation and oxidation of the remaining sulphur.

Roasting

Roasting, as applied to copper extraction, is the oxidation of the sulphide concentrates or ores. Sulphur dioxide (SO_2) is formed and emitted in the effluent gas. The degree of oxidation is controlled by regulating the supply of air to the roaster. If matte smelting is to follow, a partial roast is employed so that essentially only the iron is oxidized to allow for its elimination in subsequent stages. Enough sulphur must remain to combine with the copper in the matte. If a dead roast is desired, all the sulphur must be oxidized with excess air.

Roasting is an exothermic process. It is characterized by the fact that the heat produced after ignition temperature is reached, is sufficient for drying and preheating of the concentrates.

Current production technology is based on fine ore roasting processes since the products of beneficiation are nearly always finely ground, moist flotation concentrates. The roasting of copper concentrates takes place in either multiple hearth or fluid bed roasters. Since the 1960s, fluid bed roasters have become the preferred roaster type.

The multiple hearth roaster consists of a cylindrical vessel (Figure 2) and the concentrates pass through a number of horizontal hearths from top to bottom. Air is introduced in a countercurrent direction against the descending charge. The roasted concentrates are removed at the bottom. In Canadian plants using the multi-hearth roaster, the SO_2 concentration of the effluent gas is between 1 and 4%. This concentration is not sufficient for further processing of the effluent gas in conventional sulphuric acid plants. The flue dust in the effluent gas amounts to between 3 and 6% of the weight of the charged concentrate. Due to the high copper content of the flue dust, the dust is recovered for economic reasons. For this purpose, it is collected in flues, filters and electrostatic precipitators and recycled.

The principle of the fluid bed roaster is characterized by the fact that the concentrate is suspended in a stream of hot air (Figure 3). Approximately 75-90% of the calcined concentrate leaves the roaster in the form of flue dust which has to be recovered in dust collectors for further processing. Fluid bed roaster gases typically contain 10 to 15% SO_2.

Advantages of the fluid bed roaster are its large capacity and high reaction rates. After cooling and cleaning, the sulphur-rich roaster gases can be transferred to sulphuric acid plants for further processing, either directly or diluted with effluent gases lean in SO_2 from other production stages. The fluid bed roaster does not facilitate the rejection of volatile impurities to the same extent as the multiple hearth roaster. However, the latter produces gases of insufficient SO_2 concentration for economical sulphur recovery.

Sinter roasting is only applied in exceptional cases, producing effluent gases with a sulphur dioxide content of only 1.5 to 2.0%, making the recovery of sulphur more difficult. Both fluid bed and multi-hearth roasting are employed in Canada while sintering is not.

Matte Smelting

Smelting is a thermal treatment to melt the concentration or roaster product along with silica to bring about physical and chemical changes that allow the separation of

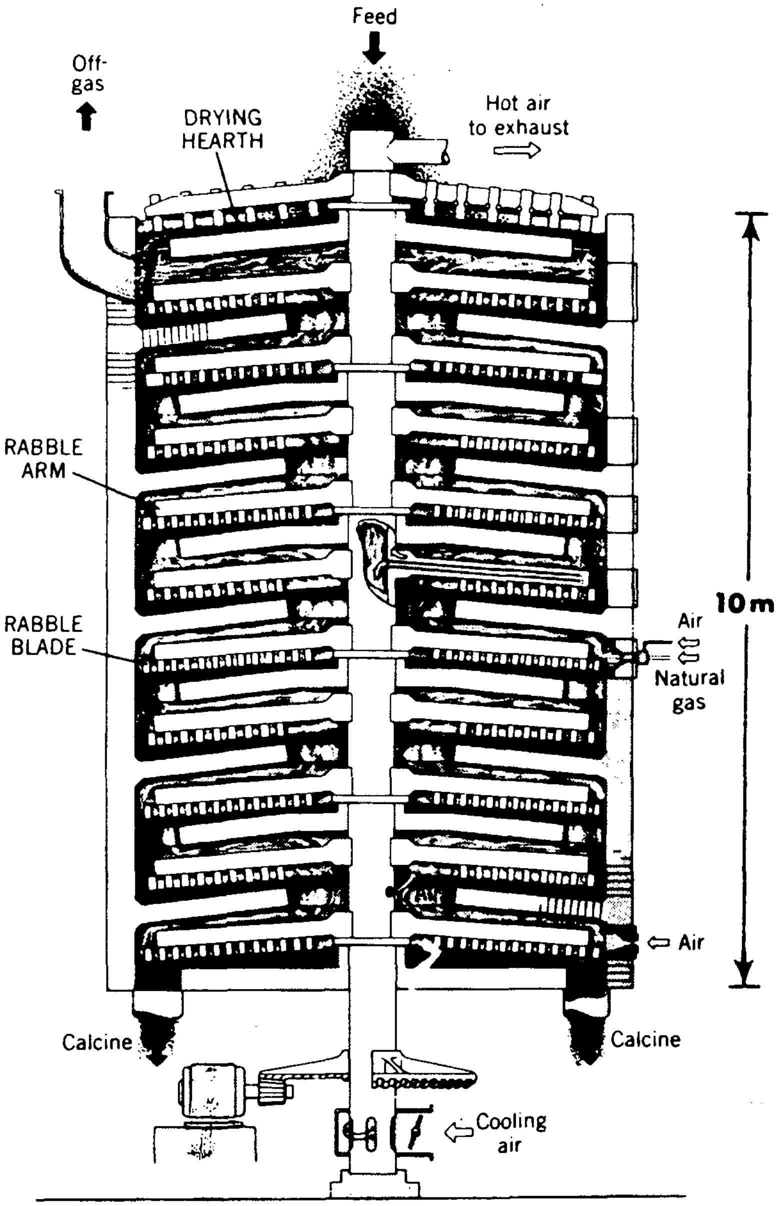


FIGURE 2 CUTAWAY VIEW OF A MULTIPLE HEARTH ROASTER

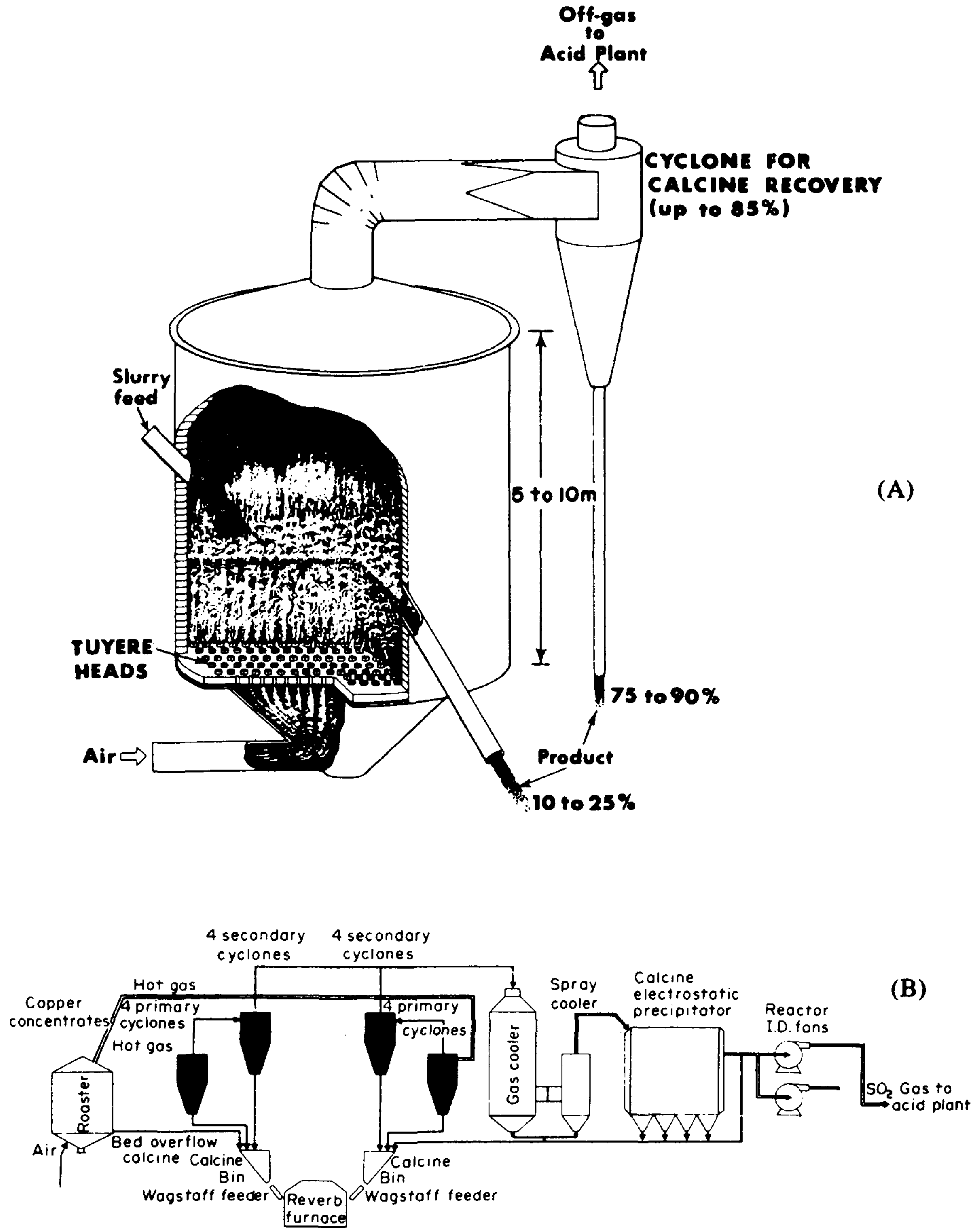


FIGURE 3 (A) CUTAWAY VIEW OF A FLUID BED ROASTER
(B) ROASTER-REVERBERATORY FURNACE FLOW SHEET (3)

the copper from unwanted materials. The iron oxide formed in the roasting stage and rock materials combine with the silica to form a fluid immiscible layer (slag) of low specific gravity which floats on top of the matte. The slag can be decanted and discarded. The sulphur, copper, the balance of the iron and most of the precious metals combine to form the matte which is tapped periodically for further processing.

Matte smelting in a shaft furnace takes place as follows: lumps of ore, briquettes or sinter material together with coke are charged in layers in the furnace throat. Air is introduced at the bottom of the furnace for combustion, thus producing the necessary temperature and partially roasting the ores. Periodically, the liquid matte is tapped and the liquid slag is skimmed. The effluent gas from the shaft furnace contains approximately 5% SO_2. The flue dust is collected in cyclones and electrostatic precipitators. The fine-grained ore concentrates usually produced nowadays are not suitable for processing in shaft furnaces. For this reason, shaft furnaces have become quite rare despite high productivity rates and good thermal efficiency (28). None are in use in Canada.

Fine-grained ore concentrates are generally smelted in reverberatory furnaces (Figure 4). The furnace is lined with silica brick or magnetite. The heat for smelting is provided by the combustion of oil, natural gas, or pulverized coal in burners situated at the front end of the furnace, producing temperatures of 1400 to 1500°C. The flame passes over the solid charge, heating it by thermal radiation. At the side facing the burner, the smelting process takes place. Slag and copper matte are separated at the end of the furnace. The slag, which is tapped at scheduled intervals, still contains 0.3 to 0.8% copper. The copper matte is tapped periodically and transported to the converter in ladles.

The thermal efficiency of the reverberatory furnace is relatively low since only approximately 25% of the generated heat is utilized (28). It is, however, still the most widely used method due to the adaptability of the reverberatory furnace to different kinds of raw materials and greatly varying throughput rates. Large amounts of effluent gas are produced during operation of the reverberatory furnace (1 300 to 1 700 Mm^3/min (9)) containing flue dust and SO_2, the latter in concentrations between 0.5 and 2%. During smelting, formation of SO_2 is unavoidable because air entering through gaps and operating openings causes a slightly oxidizing furnace atmosphere resulting in oxidation of the sulphur contained in the processed material. SO_2 is also formed due to the reduction of magnetite in the roaster product by sulphides in the reverberatory furnace matte

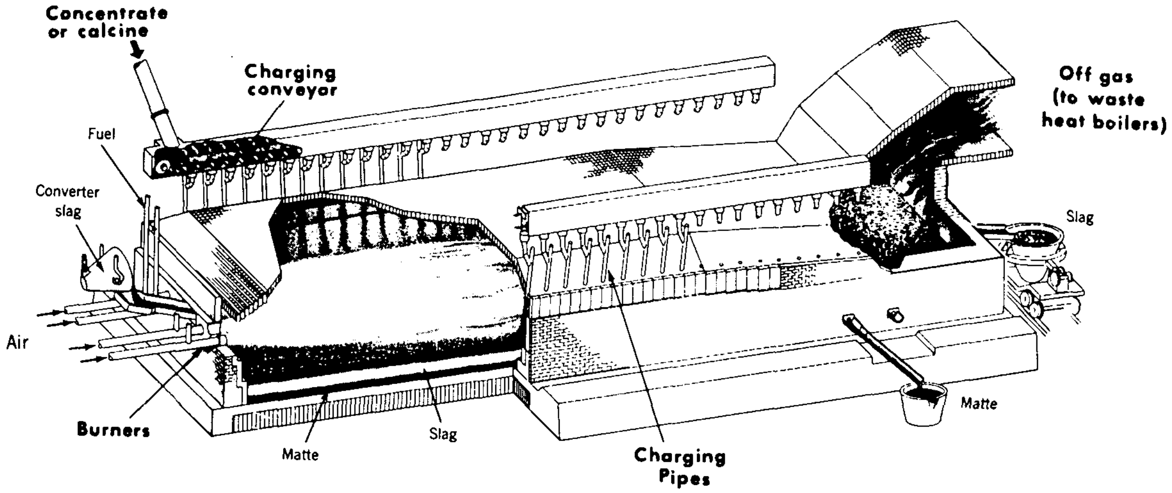


FIGURE 4 CUTAWAY VIEW OF A REVERBERATORY FURNACE (3)

($3Fe_3O_4$ + FeS → 10FeO + SO_2). In total, approximately 10% of the sulphur in the smelter feed is oxidized. The problem of purification of the effluent gas is that the concentration of SO_2 is too low for further processing (28). Present practice (in most areas) is to discharge this flue gas directly to the atmosphere after particulate collection. Newer developments of reverberatory furnaces, especially in the U.S.S.R. and in Japan, employ oxygen-enriched air and/or pre-heated air for operation in order to reduce the disadvantages mentioned above. This results in a considerable increase in concentrate throughput, a reduction in the fuel requirement (thermal efficiency 60%), and there is a reduction in the volume of effluent gases which must be treated. In special cases, it is then possible to recover the SO_2 in an acid plant (25).

In "green feed" reverberatory furnaces, unroasted, moist flotation concentrates are charged. In this case, the concentration of SO_2 in the effluent gas is higher than it is when using roasted concentrate, whereas the flue dust content is lower (8).

In the electric furnace smelting process, the roasted ore concentrates are transferred onto the liquid melt through the top of the furnace. The smelting temperature is obtained by means of electric resistance heating. Depending on the size of the furnace, 3 to 6 Soderberg anodes immersed in the liquid slag layer are used.

Advantages of an electric furnace are:

- it is versatile with regard to feed materials;
- it produces small volumes of effluent gas (containing N_2 from infiltrated air, CO and CO_2 from electrode-slag reactions and SO_2 from sulphide oxidation and magnetite reduction);
- the SO_2 concentration of its effluent gas is readily controlled by adjusting the amount of air entering the furnace.

A disadvantage of electric furnaces, however, is the high electric power consumption and it can therefore only be economically employed where the price of electric energy is low.

Converting of Copper Matte

The molten matte (copper content 30 to 65%) is charged to the converter in liquid form to produce blister copper. This process (converting) consists of the slag-forming stage and the copper-making stage.

Due to the varying affinity of the metals for oxygen, the iron contained in the copper matte oxidizes and is slagged with added SiO_2. At the same time, sulphur oxidizes into gaseous SO_2. The reaction

$$2\,FeS + 2\,O_2 + 2\,SiO_2 \rightarrow 2\,FeO \cdot SiO_2 + 2SO_2$$

is exothermic, so that the process can be operated without supplying energy. Due to the high copper content (3 to 8%), the slags are returned to the smelting furnace.

After slagging of the iron, the remaining matte usually has a copper content of more than 72% in the form of Cu_2S. In the copper-making stage, the sulphur is oxidized and escapes as SO_2. The overall reaction

$$Cu_2\,S + O_2 \rightarrow 2Cu + SO_2$$

is also exothermic, making firing with additional fuel unnecessary. The result of this process is crude copper with a copper content of 97 to 99% and varying concentrations of arsenic, antimony, lead, nickel, zinc, iron, selenium, tellurium, sulphur, oxygen, and precious metals. The small amounts of resulting copper-rich slag (20 to 40% copper content) are processed together with the subsequent charge. Table 6 shows an estimate of the distribution of impurities to blister copper, effluent gas and slag during converting (3, p. 192).

For the conversion of copper matte most smelting plants use the Peirce-Smith converter (Figure 5, 6). Charging of the liquid matte and tapping of the slag and the crude copper takes place through the mouth of the converter by rotating the converter, which is mounted on roller guides around its long axis (3, p. 186). Copper smelting plants usually operate several converters.

Large volumes of hot effluent gases are produced during the blowing periods and are collected by means of a hood over the converter opening. The space between the converter housing and the hood allows the ingress of air which dilutes the SO_2 content of the off gases. The SO_2 concentration varies depending on the process cycle. During initial blowing, SO_2 concentrations (with dilution) can be as high as 10%; during the later blowing period, and when the converter is turned away from the hood, SO_2 concentrations are much lower and often nil. The varying SO_2 concentration does not provide a satisfactory feed to an acid plant, which operates best with a relatively steady flow. This is minimized in multi-converter plants by converter scheduling to attain a relatively steady flow.

The greater the reduction of infiltrated air by well-designed close-fitted hooding and proper working practices, the higher the SO_2 concentration will be, and the more effective the acid plant will be.

The use of oxygen for enriching the blast air will also increase the SO_2 content. Water-cooled hoods are now being used in some plants to further reduce the volume of infiltration air and to provide better working conditions.

With the Hoboken converter, the large escape of effluent gas which usually occurs when the converter is tilted for charging and for tapping of slag and crude copper is avoided. The effluent gas is sucked off through a flue at the end of the converter (Figure 7). The syphon minimizes gas escape during all phases of operation. The converter is charged through a small opening at the top of the casing. Charging is also possible during blowing without tilting the converter (shorter process duration). As a result, there is a lower loss of SO_2 from the converter. Dilution of the effluent gases due

TABLE 6 DISTRIBUTION (ESTIMATED) OF IMPURITIES DURING CONVERTING (3)

	Distribution in %		
Element	Blister Copper*	Effluent Gas†	Slag
Silver (Ag)	90	0	10
Gold (Au)	90	0	10
Platinum metals (Pt)	90	0	10
Arsenic (As)	15	75	10
Bismuth (Bi)	5	95	0
Cadmium (Cd)	0	80	20
Cobalt (Co)	80	0	20
Iron (Fe)	0	0	100
Germanium (Ge)	0	100	0
Mercury (Hg)	10	90	0
Nickel (Ni)	75	0	25
Lead (Pb)	5	85	10
Antimony (Sb)	20	60	20
Selenium (Se)	60	10	30
Tin (Sn)	10	65	25
Tellurium (Te)	60	10	30
Zinc (Zn)	0	30	70

Notes:

* Not including particulate loss
† Including captured particulates and fume
The distribution depends on the copper content of the matte and on the concentration of different elements.

to infiltrated air is small. Therefore, a steadier and higher concentration of SO_2 is available than for the Peirce-Smith converter. However, the SO_2 concentration will still vary throughout the cycle. The smaller opening used for charging can create problems due to slag build-up or charging large scrap.

2.2.1.2 Specialized smelting processes. The TBRC method (Top Blown Rotary Converter) uses oxygen blown through a lance onto the surface of the bath in a vertical vessel

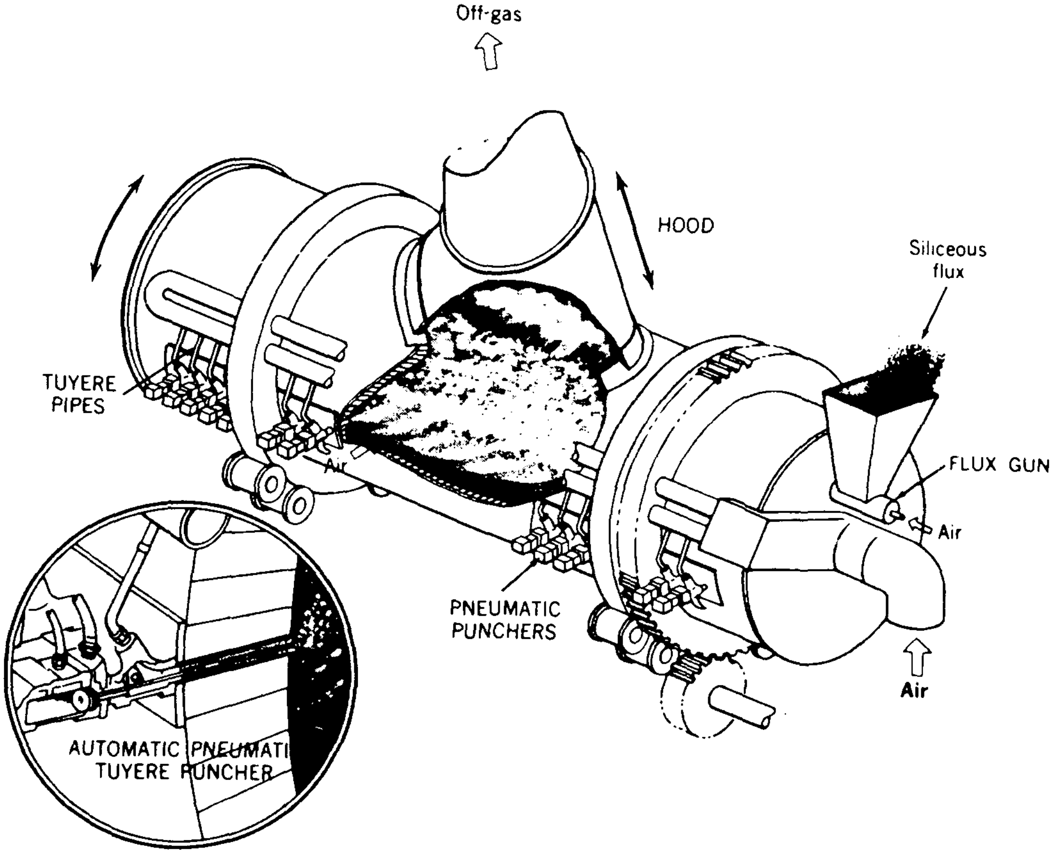


FIGURE 5 CUTAWAY VIEW OF A HORIZONTAL SIDE-BLOWN PEIRCE-SMITH CONVERTER (3)

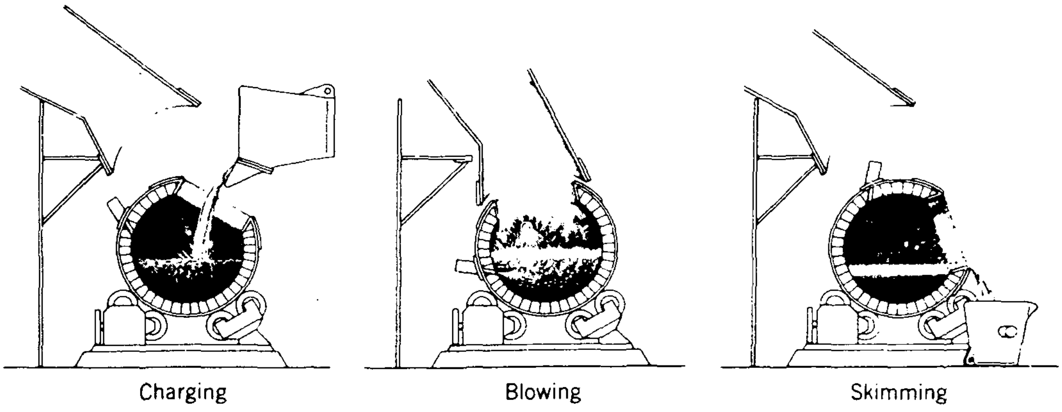

Charging Blowing Skimming

FIGURE 6 POSITIONS OF THE PEIRCE-SMITH CONVERTER FOR CHARGING, BLOWING, AND SKIMMING (SLAG OR COPPER) (3)

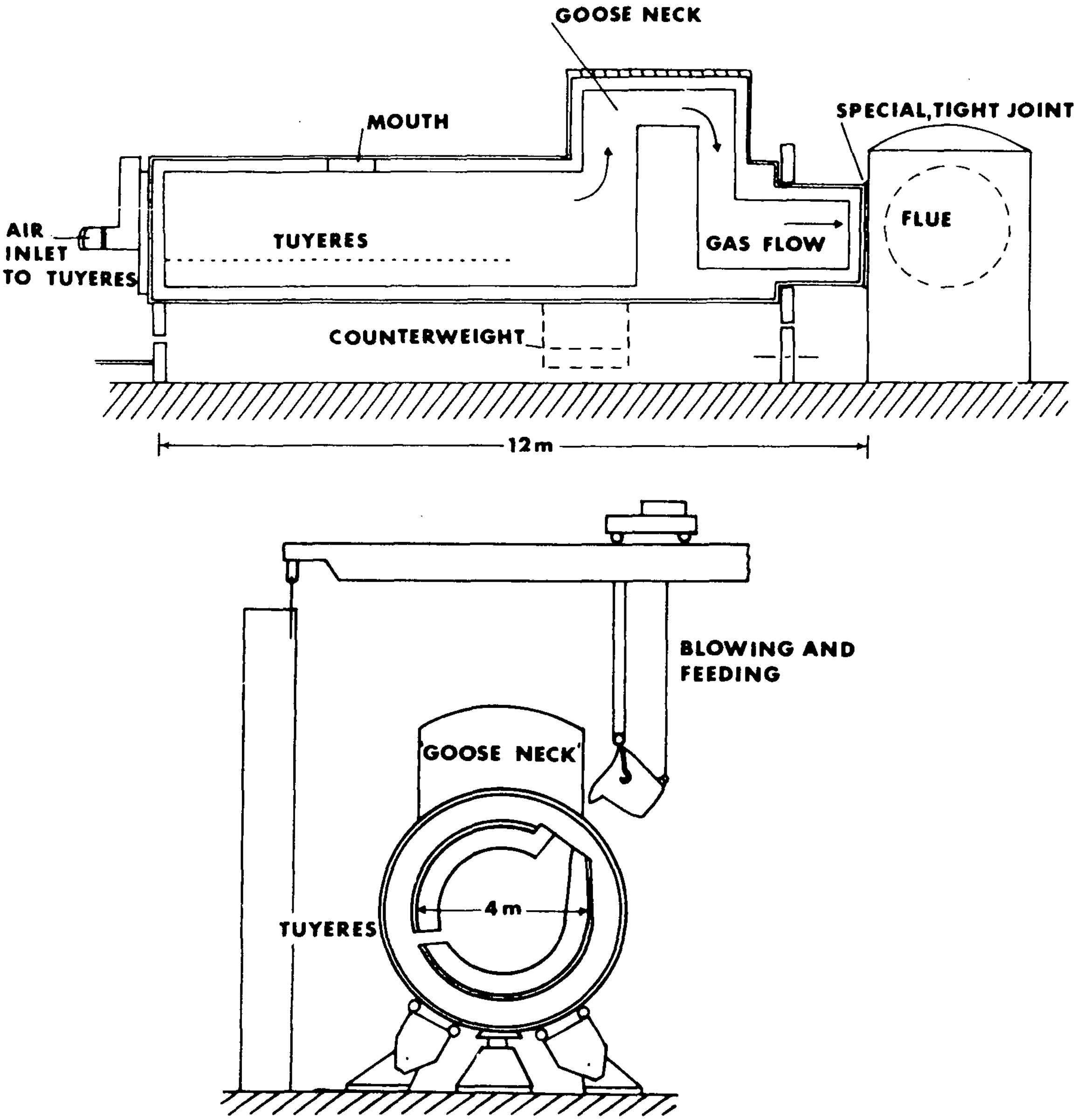


FIGURE 7 END AND SIDE VIEWS OF THE HOBOKEN CONVERTER (3)

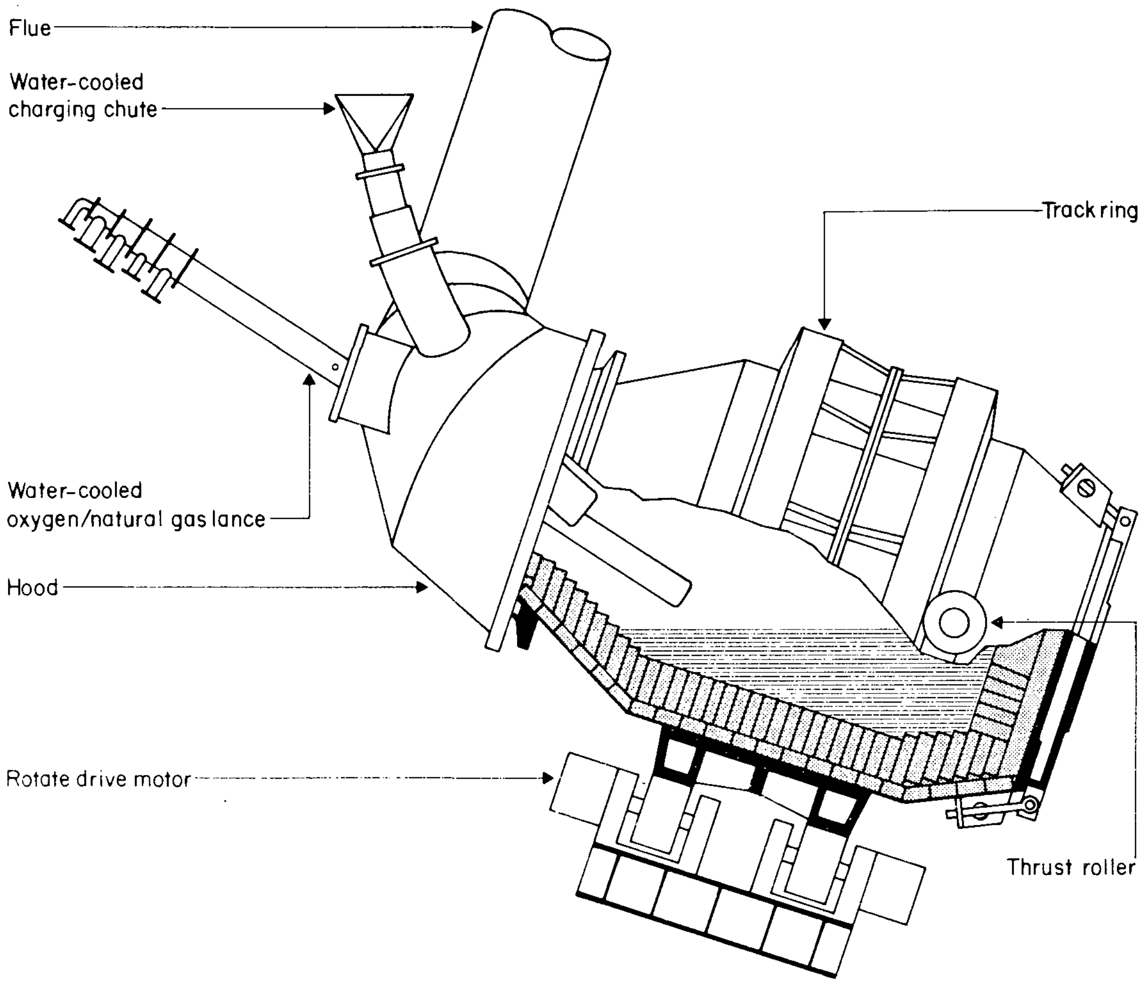


FIGURE 8 TBRC ARRANGEMENT (38)

while the vessel is rotated about its vertical axis. Figure 8 illustrates a TBRC furnace. The TBRC allows complete processing of concentrate to a fire refined copper or anode copper (40).

The vessel is equipped with two cast steel track rings which are supported within a frame by means of rollers. Rotation is imparted to the vessel through motor driven support rollers and the vessel is secured in the frame longitudinally by means of thrust rollers. The arrangement permits the vessel to rotate freely inside the support frame. The furnace is supported on trunnions so that it may be tilted through 360° for filling, blowing or emptying. When operating, the vessel is inclined at an angle, generally between 15 and 20°, to give the optimum balance between degree of fill and agitation.

The furnace has a removable bottom which facilitates refractory replacement. The mouth is equipped with an exhaust hood sealing ring which provides a bearing surface for a tight hood. The tight hood will permit SO_2 concentrations of 10 to 50% and higher at various stages of an operating cycle.

The vessel atmosphere is controlled by injection of the desired gases, such as oxygen, natural gas and air through a water cooled lance. The lance passes through the hood and can be adjusted as to both depth and angle in the vessel.

The rotation of the vessel and thus the mixing of the bath promotes a high oxygen use efficiency. The low exhaust gas volume resulting from the elimination of nitrogen and the high oxygen use efficiency will reduce the size of the exhaust gas system. The total dust in the exhaust gas is reduced not only by the low volume but also by the low emission velocity from the furnace.

The TBRC process allows: critical control of oxidizing, reducing or neutral environments; high operating temperatures; high, intermittent SO_2 concentrations in exhaust gases; low energy requirements; and reduced overall costs (47). To date, this process has only been applicable in special circumstances.

The Brixlegg process, whereby the principles of the previously mentioned methods were combined in a special way, was developed due to the special features of the ore to be treated. During this process, copper concentrates are treated in two stages to obtain iron-bearing blister copper. After complete removal of the sulphur in a fluid bed roaster (dead roasting), deoxidizing smelting of the roaster concentrate takes place in an electric furnace by adding coke breeze or bitumen-free coal. The main advantages are the emission of SO_2 at only one stage of the process and SO_2 concentrations of 8 to 10% in the effluent gas (22).

The application of further conventional processes is restricted to processing of special ores:

- rich oxidic copper ores can be smelted by reduction in the reverberatory furnace to obtain impure black copper;
- in Zambia, hard to treat oxide and banded sandstone ores are processed by means of the TORCO method. This process relies on the fact that when a non-sulphide copper ore is heated in the presence of common salt and a reducing agent, particles of metallic copper are formed. When reactor conditions are properly controlled, the metallic copper is produced in a form that can be readily recovered by conventional flotation methods.

2.2.1.3 Flash smelting process. The flash smelting process integrates the roasting and smelting processes which, by the conventional methods, are carried out in separate furnaces.

The advantages of this process include low energy consumption, high SO_2 concentration in the flue gas, high throughput and high copper concentration in the matte.

In this process, the ore concentrate and the additives are blown into a reaction chamber together with heated air, oxygen, or oxygen-enriched air and are roasted as they fall. The heat produced by the exothermic reaction is utilized for smelting of the concentrates.

Two flash smelting processes are currently in commercial use:

- the OUTOKUMPU process;
- the INCO process.

The OUTOKUMPU process has been in commercial use since 1949 (50, 51). In this process, the copper concentrates are blown into a furnace together with preheated oxygen-enriched air. The heat produced by the exothermic roasting process is utilized for smelting. Fuel is generally added to the furnace; however, when using oxygen enrichment, the furnace can be operated as a nearly autogenous system. Figure 9 shows an OUTOKUMPU flash-smelting furnace.

The OUTOKUMPU process functions as follows: the flotation concentrate is dried using either rotary kilns or suspension dryers. The waste gas from the dryer has to be cleaned in order to recover the concentrate contained in the flue dust. The cleaned gases are vented through a stack. SO_2 in the effluent gas results mainly from the use of sulphur-bearing fuel.

The dried concentrates, together with the additives and preheated air (450 to 1000°C), are blown into the furnace through nozzles at the top of a reaction tower. When using oxygen-enriched air, the preheating temperature is about 200°C.

The maintenance of a favourable temperature, adaption to varying concentrate compositions, and changes in the production rate are controlled by varying the quantity of fuel, the degree of air preheating and the amount of oxygen used.

The melted particles are separated from the gas flow and fall onto the molten bath. The matte (approximately 45 to 75% copper content (50)) is tapped at the front end below the reaction shaft and is transferred to the converter. The high copper content shortens the blowing time in the production of crude copper in subsequent processing. The

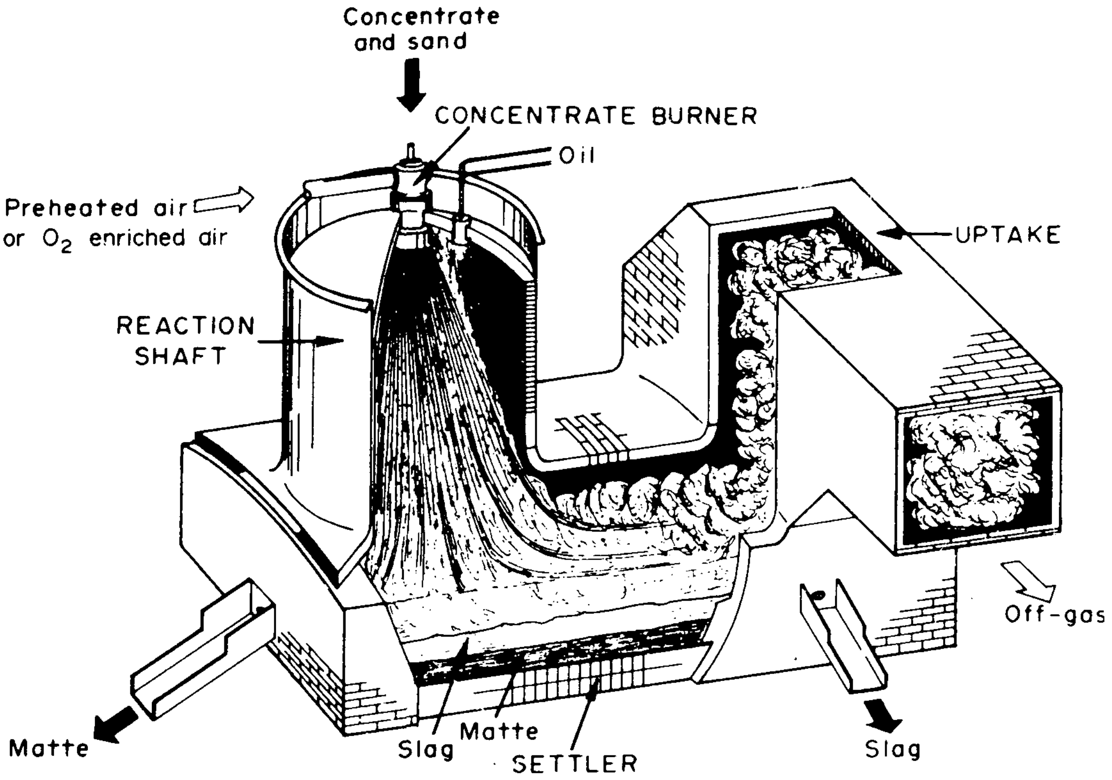


FIGURE 9 CUTAWAY VIEW OF OUTOKUMPU FLASH-SMELTING FURNACE (3)

copper-rich slags which are discharged at the other end of the furnace are processed to extract some of the copper. The extraction of copper from the slag takes place either in an electric furnace or after cooling and pulverization, by flotation - depending on the size of the smelter and different local conditions. Since the costs of subsequent treatment of the slag with low or high copper content are almost equal, the principal aim is to increase the copper content of the matte, thereby shortening the time required for blowing in the converter.

The SO_2 concentration of the effluent gases amounts to between 10 and 11% when using preheated air and over 20% when using oxygen-enriched air (51). 5 to 15% of the material charged leaves the furnace as flue dust which is recycled. In the cases where significant amounts of precious metals and toxic components are contained in the flue dust, these have to be extracted before the dust can be recycled.

The process has been modified in Japan to reduce the copper content of the slag to about 0.5% for a 45 to 50% matte grade. Subsequent treatment of this slag is unnecessary (e.g. Tamano Copper Smelter Plant, Japan) (11, p. 131). This process modification consists of introducing heat by means of electrodes in the settling area of the furnace, thereby achieving better separation of matte and slag.

Advantages of the OUTOKUMPU process compared with conventional processes are:

- high SO_2 concentration in the effluent gas;
- efficient use of energy;
- reduction of fuel consumption;
- reduction of blowing time in the converter;
- a high throughput.

Also, with the OUTOKUMPU process it is possible to make blister copper in the furnace, but that possibility is only feasible when using certain concentrates.

The INCO process has been in commercial use in one plant since 1952 (34, 37, 70). In this process, a mixture of oxygen and copper ore concentrate is blown horizontally into the furnace from both ends (Figure 10).

The concentrates are roasted and melted in the hot atmosphere of the furnace. The heat produced by roasting is sufficient for an autogenous smelting process. The slag which has a medium copper content (0.7%) flows out continuously at one end of the furnace and the matte (42% copper and 2% nickel) is tapped periodically at the centre of one sidewall. The waste gas contains 75% SO_2 and, after dust removal, is processed into liquid sulphur dioxide. The flue dust is recycled.

Section 5.3 which describes the operations at Inco Metals Co. Ltd., Copper Cliff, Canada, provides a detailed description of the Inco process.

The advantages of the Inco process are:

- very high SO_2 concentration (70-80%) in the off gas in a very low volume (typically 125-150 normal cubic metres per minute);
- efficient use of energy;
- no fuel consumption for the smelting operation;
- very high specific throughput;
- very low dusting rate (2-3% of conc.).

Also, in laboratory scale testwork, Inco has demonstrated various ways of increasing or decreasing the matte grade obtained by autogenous flash smelting. According to Inco, "There is potential for producing white metal or even blister copper in a one step smelting operation" (70).

The KIVCET method is a cyclone-furnace process developed in the U.S.S.R. This is a process for smelting complex sulphide copper concentrates in a cyclonic smelting furnace connected to a resistance-heated sedimentation hearth. The concentrates are charged into the cyclonic flash smelting chamber using oxygen. The molten copper is collected on the hearth and flows from the sedimentation chamber to the sedimentation hearth for slagging operations (12). At present, two industrial plants for processing approximately 544 tonnes and 907 tonnes respectively of copper concentrate per day are operating in the Soviet Union. Additional plants are currently in the planning or construction stage. The effluent gases from the smelting stage contain up to 80-85% SO_2 and can be used for the production of liquid sulphur dioxide.

Table 7 gives production details of industrial flash-smelting furnaces.

2.2.1.4 Continuous smelting processes. In conventional smelting processes, roasting and smelting are followed by batch converting. New developments are characterized by continuous converting so that the three steps of roasting, smelting and converting are combined in a continuous smelting process. In one development, the three steps take place in three separate furnaces with interconnecting launders and in other cases in a single furnace. The final product should be blister copper which can be subsequently treated in the anode furnace. In addition, slag with a varying copper content is produced and also an SO_2-rich effluent gas for further processing in a sulphuric acid plant. Significant advantages over conventional processes are:

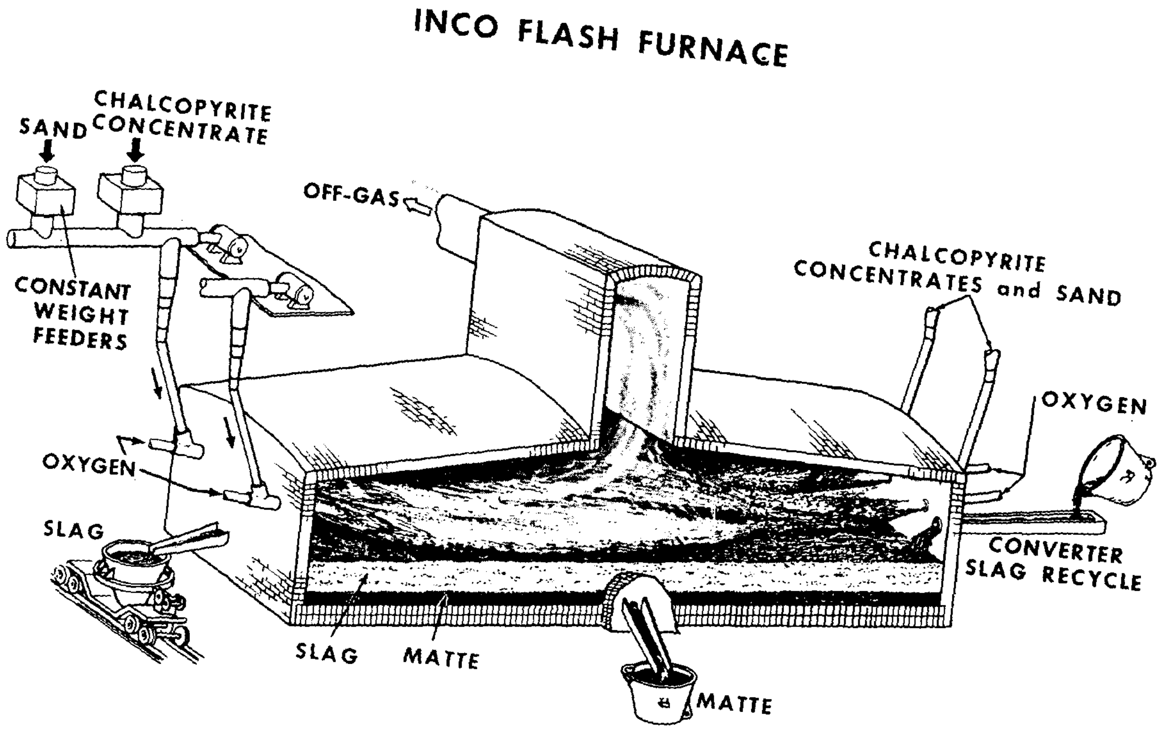


FIGURE 10 CUTAWAY VIEW OF INCO OXYGEN FLASH-SMELTING FURNACE (70)

- production of a steady flow of flue gases containing over 6% SO_2;
- improved productivity;
- improved working conditions;
- improved environmental conditions due to the reduction of fugitive emissions and the emission of SO_2 from only one source;
- lower energy requirements.

Since 1973/74, the NORANDA and MITSUBISHI versions of continuous copper-making processes have been in commercial use (3, p. 217).

The NORANDA process is currently used at Noranda in Canada and at Kennecott, Garfield, in the U.S. The process uses a cylindrical smelting furnace (Figure 11). Pelletized concentrate and additives are charged onto the bath of molten slag at the top end of the furnace. Burners fired by natural gas or oil situated at both ends, or solid fuel fed into the furnace with the feed, produce the heat necessary for processing. Oxygen-enriched air is blown into the molten bath through 60 converter tuyeres, causing sulphur and iron to oxidize. During continuous smelting in the furnace, the melt segregates into three liquid phases: slag, matte and blister copper. Due to their various densities, they settle to form three layers. The matte is tapped periodically from the bottom of the furnace and the slag flows out continuously opposite the charging end. Slag and blister copper flow in the same direction (3, p. 224), (15). This process can be used to directly produce blister copper when concentrates with low impurity levels are used. The normal operating practice at this time is to produce a copper-rich matte for further converting.

The input and output data for the NORANDA process for blister copper production is shown in Table 8 (15, p. 479). The copper-rich slag (up to 10% copper) is slowly cooled and a copper concentrate is produced by grinding and flotation. The slag concentrates and flue dust are recycled into the smelting process. The effluent gas is removed through an opening in the casing and is recovered by means of hoods. Then it is cooled to 350°C, the dust is removed and the cleaned gas can be fed into a sulphuric acid plant. The sulphur content (1.9%) of the blister copper thus produced is relatively high (15). Table 9 presents analysis results of the effluent gas during production of blister copper and matte according to the NORANDA process.

TABLE 7 PRODUCTION DETAILS OF INDUSTRIAL FLASH-SMELTING FURNACES

	INCO Process	OUTOKUMPU PROCESS (3, p. 162)			
	INCO, Canada	Tamano, Japan	Hitachi, Japan	Toyo, Japan	Harjavalta Finland
Furnace size					
W x l x h (m^2)	6 x 23 x 5	7 x 20 x 3	7 x 19 x 3	7 x 20 x 3	5 x 18 x 2
Hearth area (m^2)	138	140	133	140	90
Burner tower	none				4.2 x 7.7
Diameter x height from roof (m)		6 x 6	5.7 x 6	6 x 6	1
Concentrate burners	4	4	3	3	200^c C
Inlet air temperature	20°C (Tonnage oxygen only)	450°C	930°C	450°C	
Gas offtake					
Length x width (m)	6 x 3	2.5 diameter	7 x 3	7 x 3	7 x 3
Height (m)	6	7	6	6	6
Production details					
Type of charge	Dry concentrate (30% Cu)	Dry concentrate (30% Cu)	Dry concentrate (26% Cu)	Dry concentrate (28% Cu)	Dry concentrate (25% Cu)
Solid charge rate (tonnes/day)	(Total) 1550	(Total) 1200	(Total) 1200	(Total) 1100	(Total) 1000
Average % Cu in charge	27	24	20	25	22
Converter slag (tonnes/day)	200	None	None	None	None
Matte (tonnes/day)	940	600	550	550	340
Matte grade (% Cu)	45	47	49	49	65
Flash furnace slag (tonnes/day)	600	(500)	450	300	550
% Cu in slag	0.7	0.55	≃1	≃1	1.5
% SiO_2 in slag	32	36	34	40	27
Auxiliary Cu recovery system	None	Electric furnace within flash furnace. 0.55% Cu	Electric furnace	Electric furnace	Flotation
% Cu in final discard slag	0.7		0.5	0.45	0.4
Productivity (tonnes of charge per day/m^2)	11.2	8.6	9.0	7.9	11.1
Fuel (Bunker C oil, tonnes/day)					
Flash furnace combustion tower		37	11	32	?
Flash furnace hearth		7 plus 5.2 x 10^4 kWh/day	17	16	?
Air preheater		None	31	15 (est.)	
Charge dryers	7	7	9	None (uses waste gases)	8
Total fuel consumption	7	51 +0.5x10^5 kWh	68	63	?
Oxygen (tonnes/day)	285 (95-97% O_2)	None	40 (99.5% O_2)	None	160 (93.5% O_2)
Energy requirement including O_2 manufacture (kcal/tonne of charge)	1.1 x 10^3	4.5 x 10^5	5.8 x 10^5	5.8 x 10^5	1.2 x 10^5
Energy in auxiliary Cu recovery system			0.3 x 10^5	0.3 x 10^5	0.3 x 10^5
Total energy requirement (kcal/tonne of charge)	1.1 x 10^5	4.5 x 10^5	6.1 x 10^5	6.1 x 10^5	1.5 x 10^5

TABLE 8 DATA ON NORANDA PROCESS (15)

	Dry	% (Dry Basis)						
	Tonnes	H_2O	Cu	Fe	SiO_2	S	Pb	Zn
Input								
- Copper concentrate	5210	9.9	27.9	26.4	5.5	29.6	1.9	4.5
- Slag concentrate	1796	9.1	35.2	20.7	11.6	8.2	1.6	-
- Flux	800	3.5	0.3	4.7	68.4	-	-	-
- Precipitator dust	260	-	9.9	3.9	2.0	14.6	12.0	18.5
Output								
- Copper	1525	-	97.0	0.2	-	1.9	0.4	-
- Slag	5217	-	10.6	34.0	20.0	2.4	2.3	5.7
- Evaporative Cooler dust	100	-	54.2	7.9	5.6	13.1	1.2	3.2
- Precipitator dust	260	-	9.9	3.9	2.0	14.6	12.0	18.5

TABLE 9 ANALYSIS OF THE EFFLUENT GAS DURING PRODUCTION OF BLISTER COPPER IN THE NORANDA PROCESS

Production Alternative	Concentrations in the Effluent Gas (%)				
	SO_2	O_2	N_2	CO_2	H_2O
Production of blister copper	6.7	0.4	73.6	6.2	14.2
Production of matte	7.7	0.7	74.2	6.1	11.3

The MITSUBISHI process is currently used at Naoshima (Japan) and a second plant has been completed recently at Timmins (Canada). This process produces blister copper continually by employing three interconnected furnaces (Figure 12). (Concentrates have low impurity levels).

The dried concentrates, air, oxygen, and additives are charged into the smelting furnace by means of lances and subsequently melted to form matte (60 to 65% copper content (16, p. 447)) and slag. This mixture flows continuously through a channel

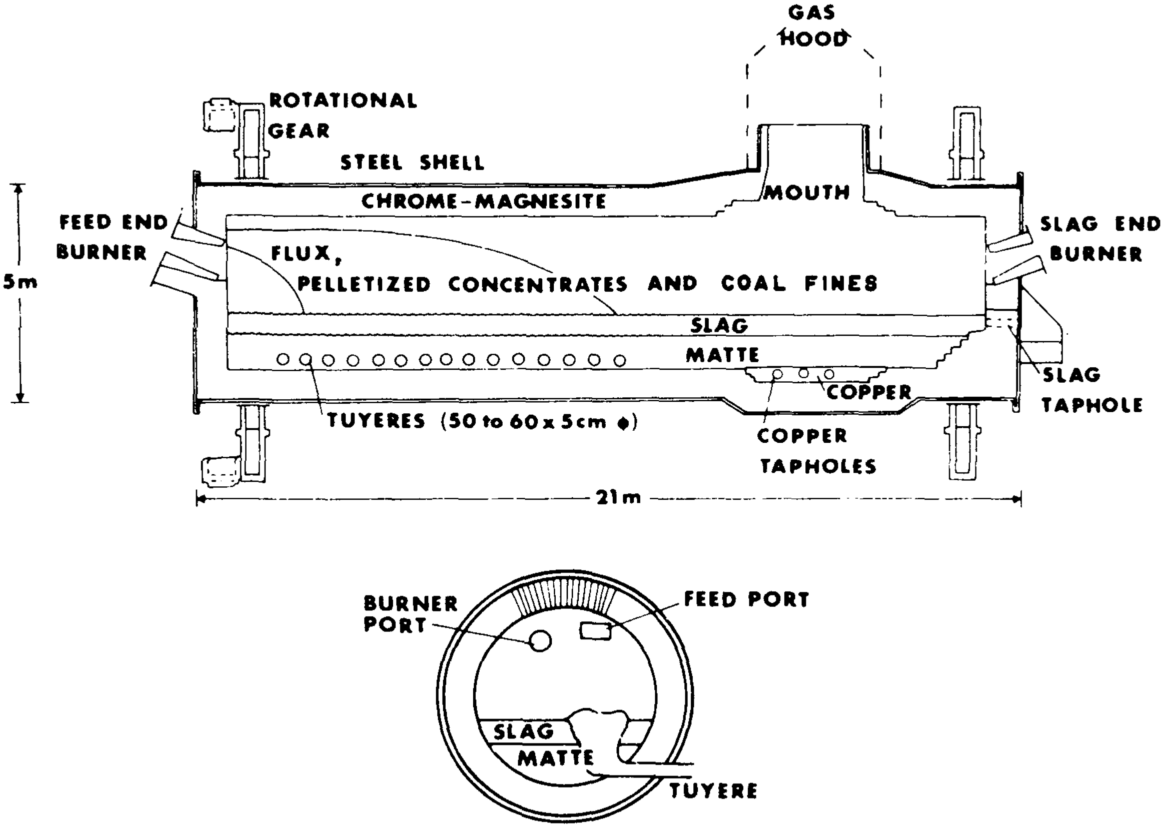


FIGURE 11 SCHEMATIC LONGITUDINAL AND END VIEWS OF THE INDUSTRIAL NORANDA SINGLE-STEP REACTOR (3)

into an electric hearth furnace which serves as a settling furnace. There the matte is separated from the slag. The slag, having a copper content of approximately 0.5%, is continuously discharged from the settling furnace. The matte flows through a syphon into the converting furnace where it is continuously processed into blister copper. Air, oxygen, and additives are blown onto the liquid bath via water-cooled lances. The blister

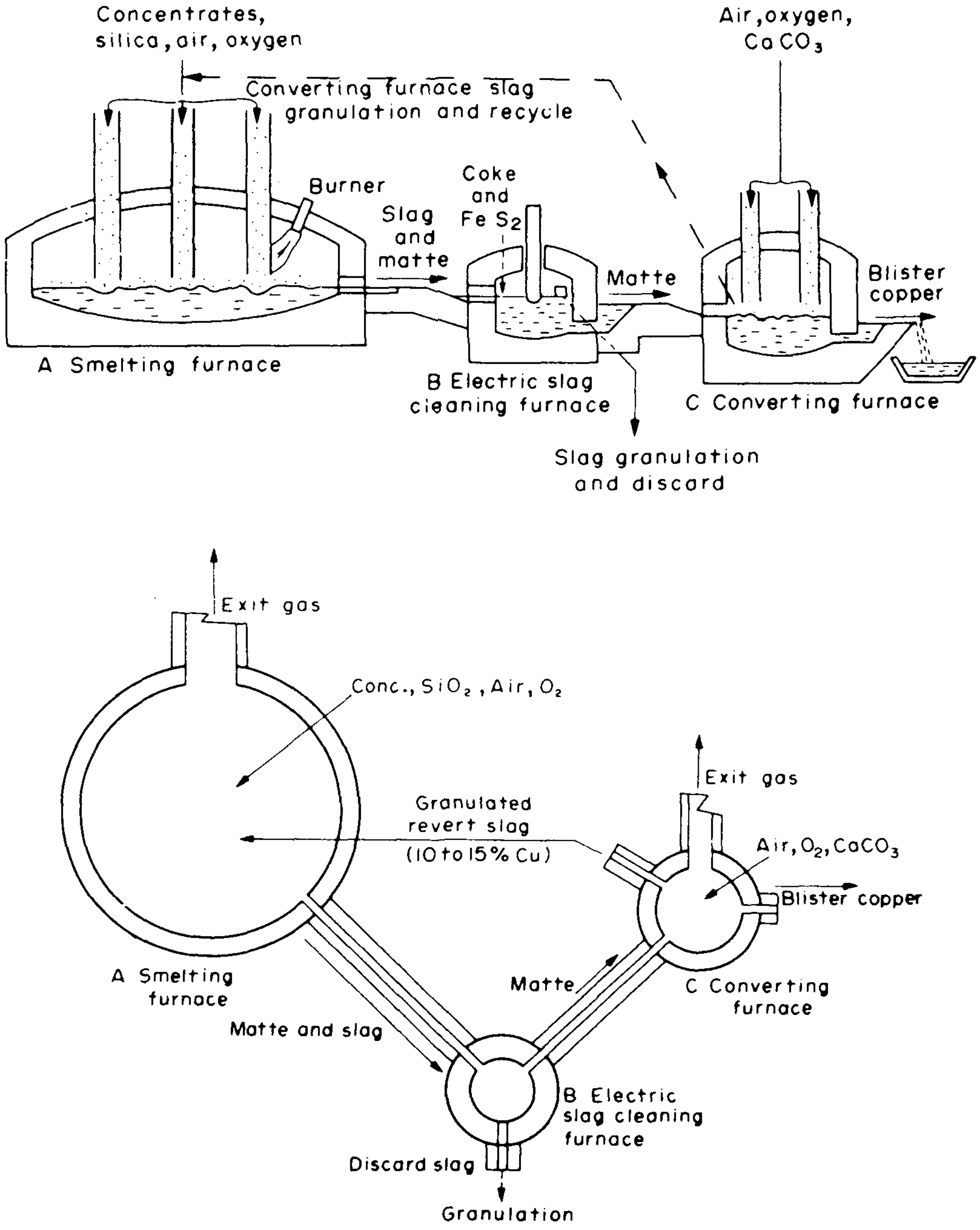


FIGURE 12 SCHEMATIC VIEW OF THE MITSUBISHI SMELTING FURNACE LINE (3)

copper thus produced contains approximately 98.5% copper and only approximately 0.05% sulphur. The extremely low sulphur content results in small quantities of SO_2 emissions during further processing of the copper. The converting furnace slags (17.6% copper content) are recycled to the smelting furnace.

The effluent gases produced in the smelting furnace and in the settling furnace contain approximately 10% SO_2.

The WORCA process has only been developed to the pilot plant stage. In this process, the furnace consists of a smelting zone, an oxidation zone and a slag settling zone. The slag is discarded at the same place as the concentrate is melted, because there the slag still has a low copper content. The slag produced in the oxidation zone also flows to the slag settling zone in countercurrent direction towards the matte. Blister copper was produced in the pilot plant (19, 29, 32) and the SO_2 concentration in the flue gas was approximately 5% (Figure 13).

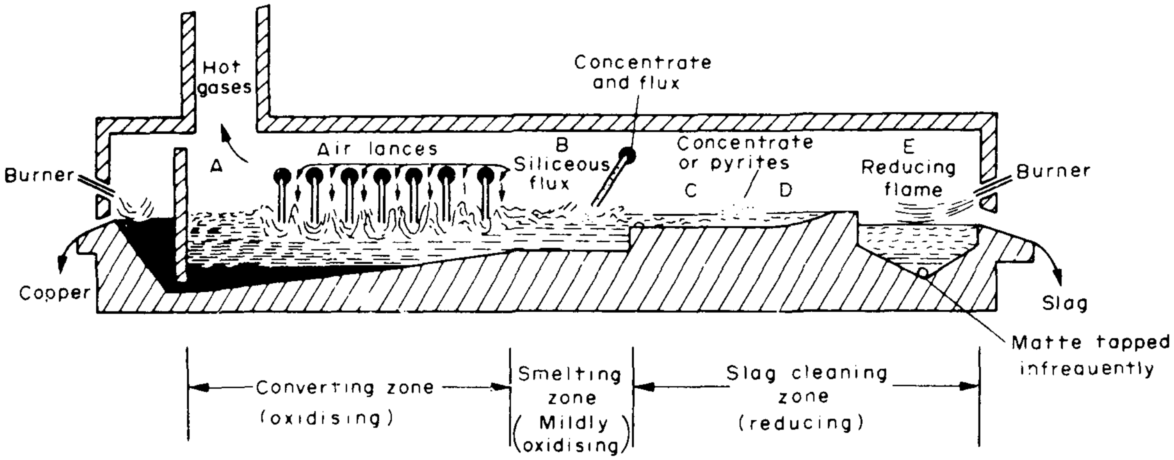
2.2.1.5 Energy requirements of smelting processes. The minimization of energy use is becoming increasingly important as hydrocarbon fuel prices increase. Table 10 examines the energy requirements of smelting processes as of 1978. These energy data include the energy required to smelt, to manufacture O_2 and to recover copper from slag, but they do not include waste heat credit or acid plant energy requirements which by and large offset each other. It can be seen that INCO oxygen flash smelting and oxygen enriched autogenous Outokumpu smelting are the lowest overall energy consumers (42).

Perhaps the clearest point to come out of the 1970's is the role of pure oxygen in lowering energy consumption. Virtually every study concludes that energy which is spent in producing oxygen pays dividends in lowering overall energy consumption (47, 48). This is because the energy produced by oxidizing sulphur and/or iron with pure O_2 far exceeds the energy required to make the O_2, thus making it energetically profitable to replace hydrocarbon fuel with oxygen wherever physically possible.

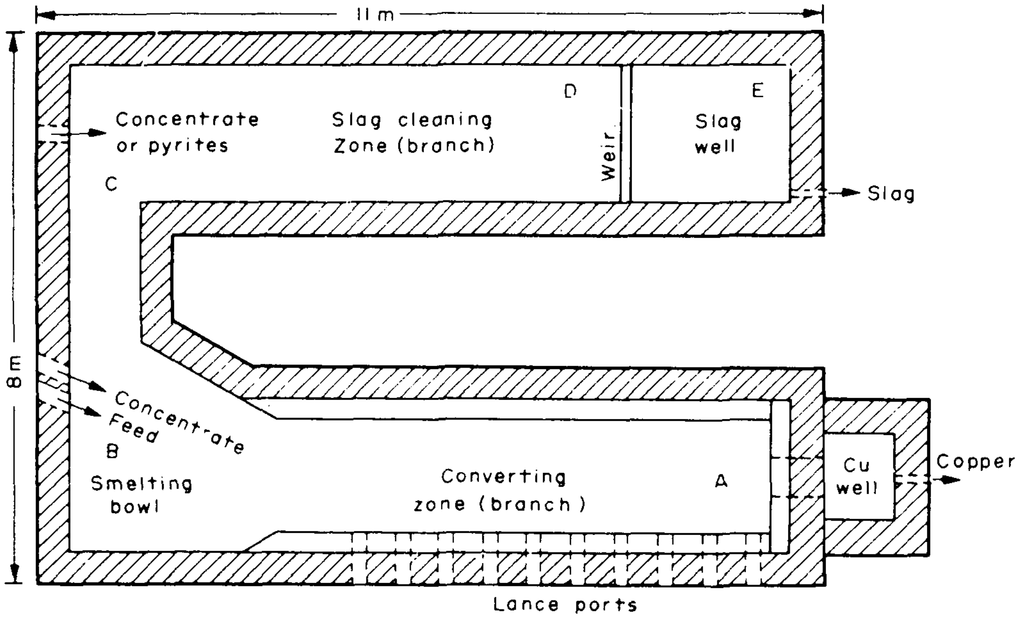
2.2.2 Hydrometallurgical Processes. In the Western world, 0.9 to 1.1 million tonnes of copper are presently being produced by hydrometallurgical techniques. These processes are mostly used for the recovery of copper from lean oxide raw materials and rich sulphide concentrates.

Hydrometallurgical processes consist of three production stages:

- leaching i.e., dissolution of the copper components from the gangue,
- enrichment or purification of the copper solution;
- separation of the copper.



(a) Elevation view†



(b) Plan view

FIGURE 13 PLAN AND ELEVATION VIEWS OF WORCA-PROCESS PILOT REACTOR (3)

TABLE 10 ENERGY USED BY VARIOUS COPPER SMELTING PROCESSES (42)

Furnace	Type of operation	Hydrocarbon fuel energy kJ/tonne of charge	Electrical energy kJ/tonne of charge
Flash			
INCO	Oxygen flash	4×10^5	3×10^5
Outokumpu	Autogenous, O_2	4×10^5	4×10^5
Outokumpu	Hot air blast	23×10^5	1×10^5
Electric	Dry concentrate	4×10^5	14×10^5
	hot calcine		9×10^5
Noranda	31% O_2, blister	13×10^5	2×10^5
Mitsubishi	30% O_2, blister copper	16×10^5	2×10^5
KIVCET	Pure O_2, electric zinc reduction	4×10^5	12×10^5

Figure 14 shows the processing steps of industrial leaching and copper-recovery processes.

Selection of the appropriate solvent and leaching process is chiefly dependent on local conditions and on the composition of the copper-bearing raw material.

Separation of the copper from enriched solutions takes place either by cementation or solvent extraction. Cementation is the separation of copper from leach solutions by precipitation, principally with iron. The copper which precipitates on the iron surface is mechanically separated.

Cement copper usually contains 85 to 90% copper, 0.2 to 2% iron, 0.5% silica (SiO_2), aluminum oxide and other metallic components. Further processing of the cement copper is predominantly carried out by pyrometallurgy.

Solvent extraction is a process for the extraction of copper ions from dilute solutions. The significant stages of this process are:

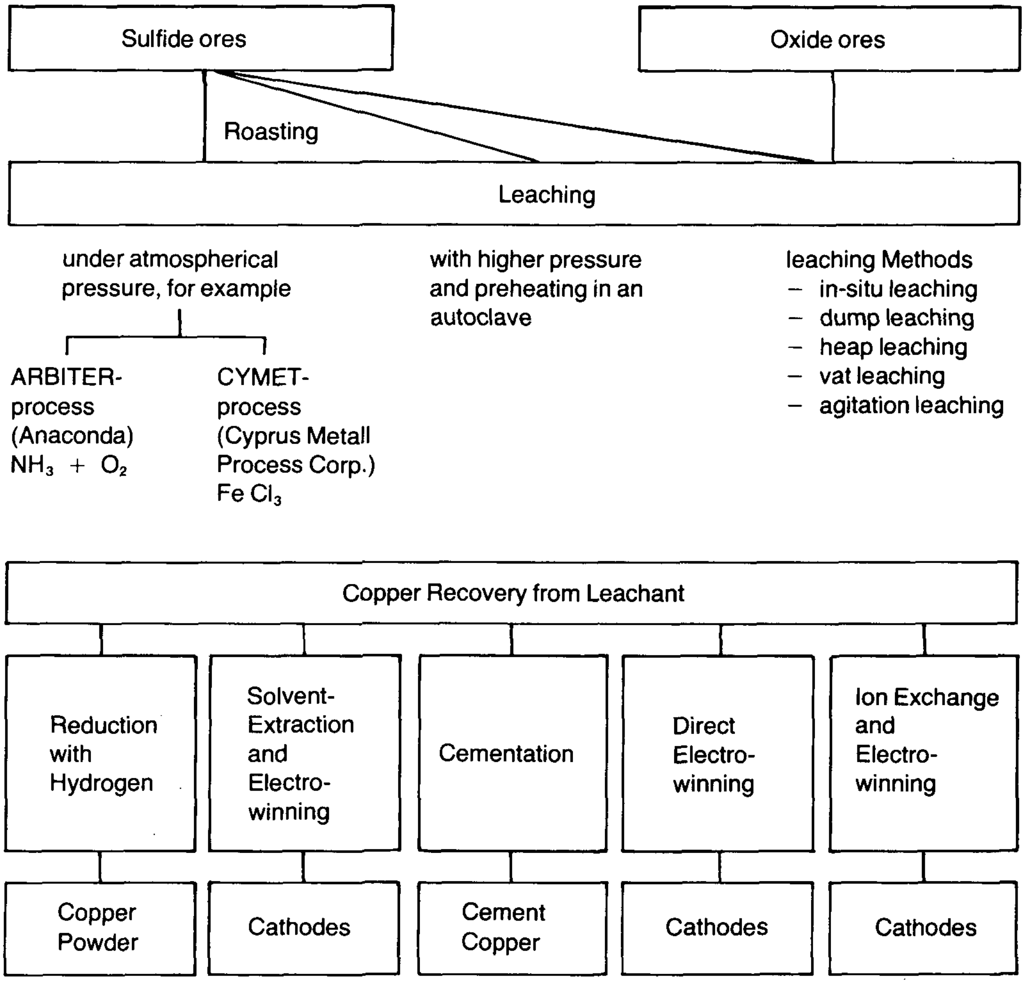


FIGURE 14 FLOW SHEET FOR INDUSTRIAL LEACHING AND COPPER RECOVERY PROCESSES (14)

- separation of the copper from an acid solution into an organic phase;
- separation of the copper from the organic phase by a strong acid (e.g. sulphuric acid) the liquid thus formed contains a sufficient concentration of copper which may be recovered by further processing.

2.2.2.1 Leaching methods. Copper ores with a low copper content (< 0.3%) may be leached in situ, i.e., at the site of their occurrence.

In the in situ leaching process, leachant (acid containing liquor) is directly introduced to the ore by spraying. The copper is leached out of the ore over a period of time and the copper-rich leachant is recovered for further processes.

In the dump leaching process, the oxide and sulphide residues from open pit mining are placed in large piles. The leachant is distributed over the surface of the pile by sprinkling or flooding, and the copper-rich leachant is collected from under the pile for further processing.

The heap leaching process is similar to the dump leaching process, but is mainly used for lean porous oxide ores.

In the vat leaching process, crushed ore is leached in a vat. It is normally used only for oxide ores due to the short leaching time. The recovery can be increased by the use of agitation and/or increased temperature.

Leaching of roasted sulphide concentrates is practised in some smelting plants in Zaire and Zambia. The SO_2-bearing gases which are produced during sulphatizing roasting of the concentrates are processed to produce sulphuric acid. The sulphuric acid in turn is used as a leachant. Generally, oxide copper ores or copper ore concentrates are leached together with roaster concentrates.

In Table 11 details of the most significant leaching methods are compared.

2.2.2.2 Leaching of oxide and sulphide copper ores. Where oxide ores contain calcareous or dolomitic gangue, ammonia can be used for leaching. (Figure 15).

A large number of process combinations for leaching of sulphide ores have been investigated. Very few have been developed into commercial processes. The applicable leaching agents include ammonia, sulphuric acid, chlorine, nitric acid, and hydrochloric acid. In some cases, sulphide copper ores can be leached without previous treatment. Usually, however, they are pretreated, e.g., by grinding to a certain grain size, by activating leaching with ferric sulphate, by various roasting methods to achieve partial or complete oxidation or by bacterial leaching.

TABLE 11 DETAILS OF LEACHING PROCEDURES FOR HYDROMETALLURGICAL COPPER EXTRACTION (3)

Leach method	Mineralization	% Cu in ore	H_2SO_4 concentration in leachant (kg m^{-3})	Cu concentration in pregnant solution (kg m^{-3})
In-situ	Oxide (with some sulphide)	0.5-1	1-5	1-2
Dump	Oxide/sulphide mine wastes	0.2-1	1-5	1-2
Heap	Oxide	0.5-1	2-10	2-5
Vat	Oxide	1-2	2-10	30-40
Agitation	Oxide (concentrate)	20-30	50-100	30-50
	Roaster calcines	30-40	50-100	30-50

Two ammoniacal leaching processes are used commercially. The Sherritt-Gordon process is used for copper-nickel sulphide concentrates while the ARBITER process is used for copper sulphide concentrates. Figure 16 shows a flow sheet for the ARBITER process.

A number of processes have been developed using chloride leaching. The CLEAR process developed by the Duval Corp. is used in a plant in Arizona. In the CLEAR process, chalcopyrite is oxidized by ferric chloride to cupric chloride, ferrous chloride and elemental sulphur. The cupric chloride is reduced to cuprous chloride by cement copper prior to electrolysis to recover copper. Ferric chloride is regenerated by oxidation. Figure 17 is a flow sheet of the CYMET process which is another process using chloride leaching.

The Roast-Leach-Electrowinning (R-L-E) process is used commercially in Arizona, Zambia and Zaire. The sulphide ore concentrates are sulphatized in a fluid bed roaster prior to leaching.

A survey of selected leaching processes is presented in Table 12.

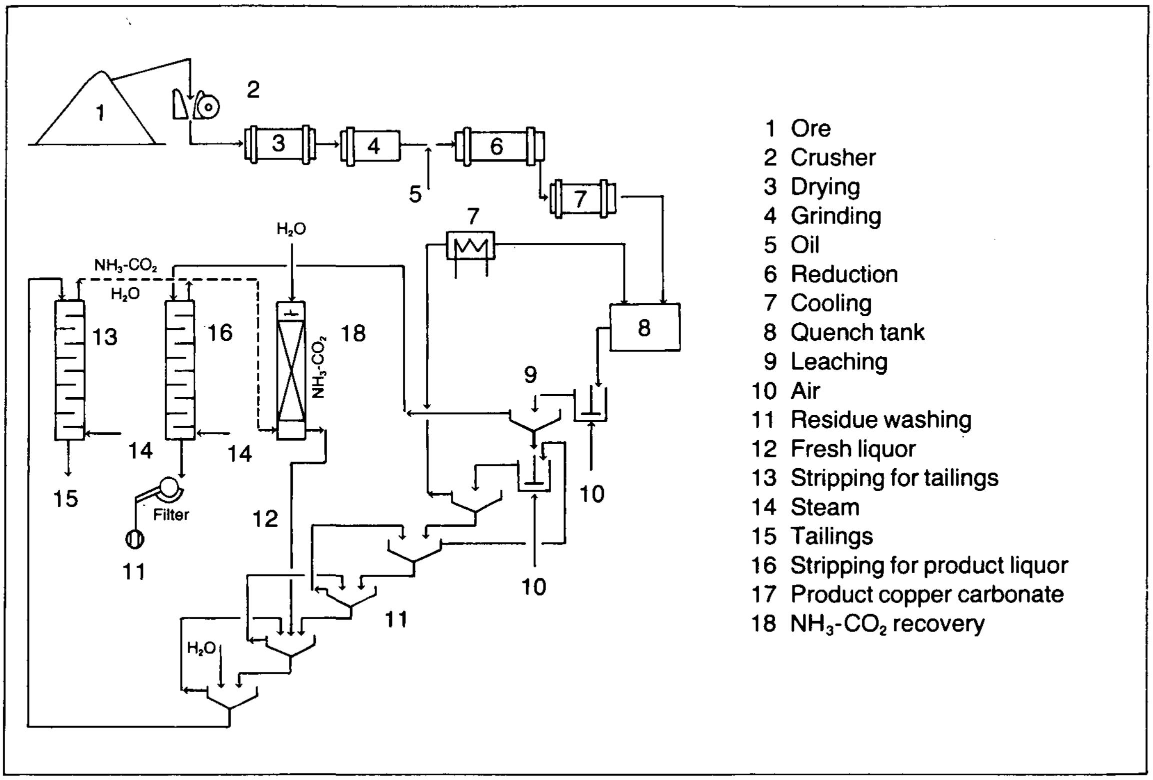


FIGURE 15 PRINCIPAL FLOW SHEET OF NICARO PROCESS APPLIED TO OXIDIC COPPER ORES (52)

2.2.3 Refining

2.2.3.1 Fire refining. Blister copper produced by conventional processes contains approximately 0.03 to 0.05% sulphur, 0.5% oxygen and impurities such as arsenic, antimony, selenium, tellurium, and precious metals. Blister copper from continuous smelting processes will contain 0.5 to 2% sulphur and up to 2% oxygen (3, p. 242), (29).

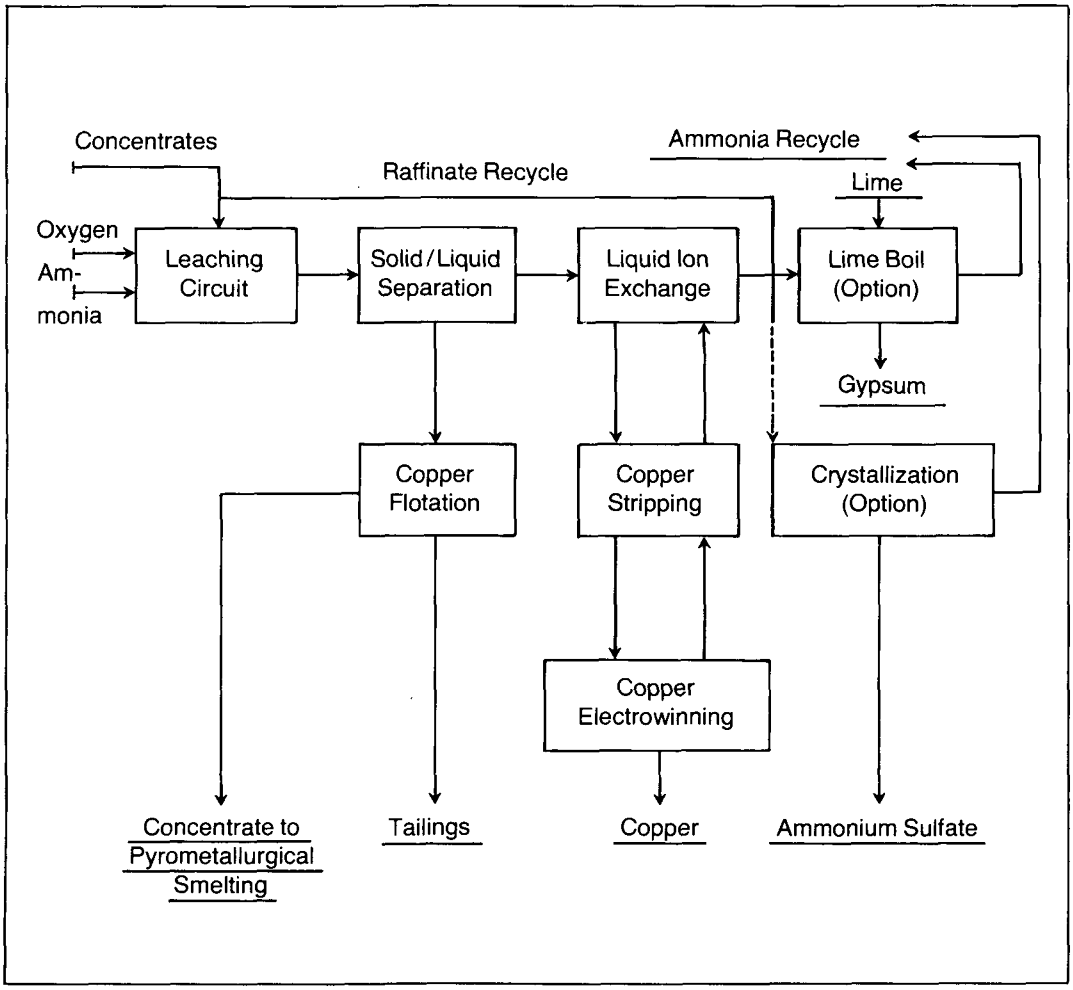


FIGURE 16 FLOW SHEET - ARBITER PROCESS (7)

The impurities in the blister copper are reduced by fire refining in preparation for the electrolytic extraction of copper. It is carried out in two steps:

- oxidation of the impurities contained in the copper;
- reduction of the oxygen in the copper by means of hydrocarbons.

In some copper-smelting plants, fire refining is carried out in small hearth furnaces. The furnaces are fired with coal, oil, or gas. The air necessary for oxidation, and hydrocarbons for reduction are introduced via steel lances which are submerged into the molten bath. In some plants the gaseous hydrocarbons are replaced by wooden poles.

Table 13 gives examples of the concentration of sulphur, oxygen, and hydrogen at various stages of refining (3, p. 243).

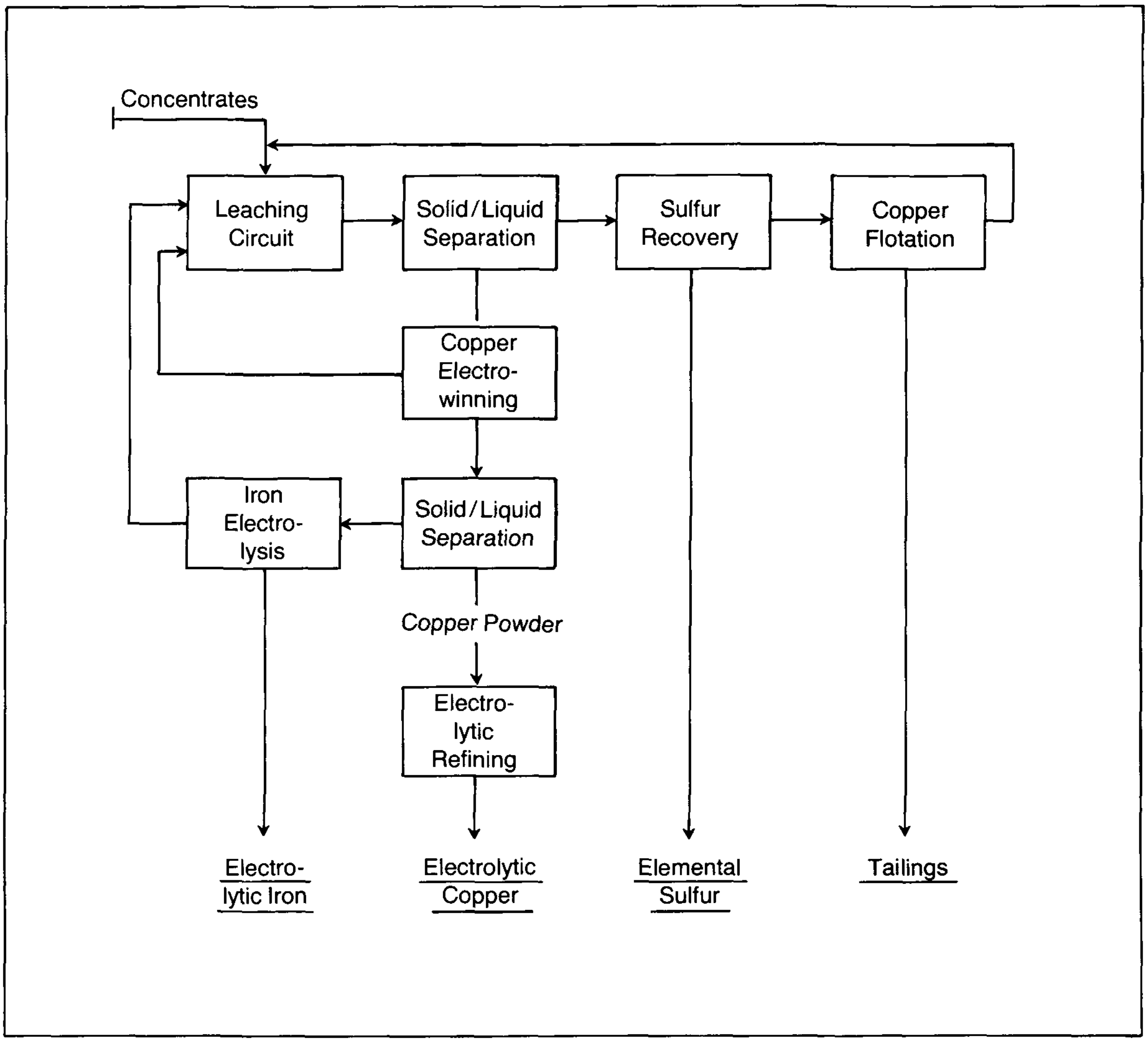


FIGURE 17 FLOW SHEET - CYMET HYDROMETALLURGICAL PROCESS (7)

Barrel furnaces, similar to the Peirce-Smith converters, are used in new plants for fire refining. Air is introduced into the molten bath through nozzles (5 to 15 Nm^3/min) for oxidation. During the reduction phase, gaseous hydrocarbons are introduced through the same nozzles until the oxygen content is reduced to approximately 0.05 to 0.2%. After completion of the refining procedure, the liquid metal is covered with low sulphur coke to prevent reoxidation of the copper (3, p. 245). The Tojo copper smelting plant in Japan employs ammonia as a reducing agent (23).

The refined copper is cast into square anodes. In modern plants, the anode casting is fully mechanized.

The quantities of effluent gas and the dust contents resulting from refining vary according to the operation. The effluent gas leaves the furnace at a temperature of about 1000°C. The flue dust contains soot, metal, and metal oxide particles.

TABLE 12 SURVEY OF SELECTED LEACHING PROCESSES

Name of Process	Leachant	Development	Reference
OXIDE ORES:			
Nicaro Process	Ammonia	Experimental State	52,53
SULPHIDE ORES:			
Arbiter Process	Ammonia	Industrial Use	19,7,54,
Double-Roast Leach Process	Ammonia	Experimental State	55
CLEAR Process	Chloride	Industrial Use	56,57
Cymet Process	Chloride	Pilot State	19,7
Sherritt-Gordon Cominco (S-C) Process	Sulphuric Acid	Pilot State	49
Roast-Leach-Electrowinning (R-L-E) Process	Sulphuric Acid	Industrial Use	58,21,54
Anatred Process	Sulphuric Acid	Pilot State	62
Cisro Process	Magnesium Sulphate	Experimental State	
Du Pont, Kennecott	Nitric Acid	Pilot State	59
SULPHIDE-OXIDE AND COMPLEX ORES:			
Leach-Precipitation-Flotation (L-P-LF) Process	Sulphuric Acid	Industrial Use	30
Lurgi-Mitterberg Process	Sulphuric Acid	Pilot State	60
San Telmo Process	Sulphuric Acidic-ferric sulphate	Pilot State	61

TABLE 13 SULPHUR, OXYGEN AND HYDROGEN CONCENTRATIONS AT VARIOUS STAGES OF FIRE REFINING (3)

Stages of the Process	Weight % S	Weight % O	Weight % H
Blister Copper	0.02 - 0.1	0.5 - 0.8	-
After Oxidation	0.001 - 0.003	0.6 - 1.0	-
After Reduction "poling"	0.001 - 0.003	0.05 - 0.2	2×10^{-5}
Anode Casting	0.001 - 0.003	0.05 - 0.3 (as Cu_2O)	1×10^{-6}

SO_2 emissions from fire refining arise from the oxidation of the sulphur in the blister copper and the fuel. SO_2 emissions will be higher when refining blister copper from continuous smelting processes.

2.2.3.2 **Final refining.** The copper anodes produced by fire refining still contain some impurities such as bismuth, nickel, arsenic, antimony, precious metals, etc. in varying amounts. The final refining of this copper is carried out in an electrolytic process. The refined copper in the form of cathodes is remelted and cast in the required form for market.

3 EMISSIONS TO THE ATMOSPHERE

3.1 Emissions from Ore Preparation and Beneficiation

Blasting, transportation, and comminution of the ore produce emissions of dust. Some of these emissions, especially those from the blasting and transportation of ore in open pit mines, are of a fugitive nature. When wet grinding is carried out, the emissions from the grinder will be very small. However, the emissions from dry grinding will be large. Emissions of particulate matter will also be produced by the concentrate drying operations. Some SO_2 will be emitted from the sulphur in the fuel, by drying operations and in some cases from the partial oxidization of the sulphides. In some cases, especially in arid areas, fugitive particulate emissions from the tailing disposal areas may be a serious problem.

3.2 Emissions from Copper Smelting

The pyrometallurgical processes for the production of copper produce large quantities of particulates and SO_2. The composition of the particulates will vary from plant to plant, depending on the composition of the concentrate and the smelting processes used. Some pollutants such as arsenic and mercury are especially difficult to control. The newer smelting processes, such as flash smelting, and continuous smelting produce emissions from a smaller number of sources and concentrations of SO_2 which are more amenable for collection.

3.2.1 Roasting. The traditional roasters such as the multiple hearth produce emissions with an average of 1 to 4% of SO_2 and 3 to 6% of the weight of the charged concentrate as particulate. This type of roaster also produces substantial amounts of fugitive emissions. The fluid bed roaster, which is now becoming more common produces emissions with an average of 10 to 15% SO_2; up to 80% of the calcine concentrate will leave the roaster in the flue gas. 80 to 90% of the particulate is recovered by the cyclones associated with the roaster as particulates and 99+% of the remainder is recovered by electrostatic precipitators. A portion of the volatile substances such as arsenic and mercury will remain in the flue gas.

3.2.2 Smelting. The traditional smelting unit has been the reverberatory furnace. The emissions from this furnace will normally contain 1 to 2% SO_2 which can be increased to 2.5% by oxygen enrichment of the air. The gas emitted also contains substantial particulate matter. The electric furnace smelting unit has a higher SO_2 concentration and a much lower volume of emissions than the reverberatory furnace.

Flash smelting produces SO_2 concentrations as high as 80% when only oxygen is used, or 10 to 15% when no oxygen is used.

3.2.3 Converting. The conventional Peirce-Smith converter produces emissions with SO_2 concentrations varying from 0 to 10% and averaging about 4 to 5%. There are also particulates and volatile elements such as arsenic in the flue gas. This converter is also a source of fugitive emissions (66). The Hoboken converter has emissions similar to that of the Peirce-Smith converter except that the SO_2 content is usually higher and the fugitive emissions are less.

3.2.4 Continuous Smelting. The continuous smelting process produces emissions with a higher and more steady SO_2 concentration ranging from 8 to 14% when oxygen enrichment is used. Particulates in the flue gas are substantial. Fugitive emissions are minimized since all operations take place in closed vessels.

3.2.5 Miscellaneous. The miscellaneous emissions include particulates and SO_2, mainly from the transport and handling operations of molten metal.

3.3 Hydrometallurgical Processes

The major emissions from the hydrometallurgical processes will be gases from leaks and open tanks throughout the plant. Among these are ammonia and hydrogen sulphide.

3.4 Refining

Some dust and SO_2 will be contained in the emissions from the fire refining furnaces. The SO_2 concentration will be higher when refining blister copper from continuous smelting processes. Some acid fumes will be emitted from electrolytic refining, and if the concentration of arsenic builds up in the electrolyte, arsine gas will be formed and emitted.

4 AIR POLLUTION CONTROL TECHNOLOGY

4.1 Control of Emissions from Ore Preparation and Beneficiation

Fugitive particulate emissions from tailings disposal areas can usually be controlled by revegetating inactive areas (72,73,74) and by wetting active areas. The fugitive emissions from the transport of the ore can be reduced by controlling the dust on the roadways with water. The particulate emissions from crushing and dry grinding can be controlled by fabric filters or wet scrubbers.

4.2 Control of Emissions from Copper Smelting

Table 14 gives uncontrolled emissions of SO_2 from roasting, smelting and converting processes. Particulates in amounts up to 5% of feed can also be emitted. The various control methods are described in the following sections.

4.2.1 **Roasting.** The SO_2 concentration in the roaster gas emitted from the multiple hearth roaster is too low for economic recovery of sulphur with present technology. The gases emitted by the newer fluid bed roasters is sufficiently rich to be treated in sulphuric acid plants for the production of H_2SO_4. The particulates must be removed from the flue gas before it is treated in the acid plant. The usual equipment is electrostatic precipitators followed by acid scrubbing. Some of the volatile pollutants such as arsenic and mercury may create problems and may have to be removed before the flue gas is treated in acid plants. The waste effluent from the acid scrubbing will create water pollution problems unless adequately treated.

4.2.2 **Smelting.** The SO_2 concentration from the reverberatory furnace is too low for the conventional sulphuric acid plant. In some special cases where a local problem exists, the SO_2 has been concentrated into a richer stream by chemical absorption processes. The particulate from the reverberatory furnace is normally removed by high efficiency electrostatic precipitators. The SO_2 concentration in the emissions from flash smelting furnaces is sufficiently rich in SO_2 for H_2SO_4 production or, as in the case of the Inco furnace, liquid SO_2. The particulate collection is similar to that of roasting where sulphuric acid is produced.

4.2.3 **Converting.** The varying SO_2 concentration from either the Peirce-Smith or the Hoboken converters is not normally a good feed for a H_2SO_4 plant. However, where the plant is a multi-converter operation, the converters can be scheduled to provide a

TABLE 14 CONCENTRATION OF SULPHUR DIOXIDE IN EMISSIONS FROM VARIOUS ROASTING, SMELTING, AND CONVERTING PROCESSES WITHOUT CONTROL

Plant Process	SO_2%
Roasters	
Multiple Hearth	1-4
Fluid Bed	10-15
Smelting Furnaces	
Reverberatory	
Calcine charge	0.5-1.5
Green charge	1.5-2.5
O_2 enriched	2.0-3.0
Electric	3-4
Brixlegg	8-10
Flash	
Outokumpu	10-15
INCO	75-80
KIVCET (O_2 enriched)	80-85
Continuous	
Noranda	
No O_2 enrichment	4-5
O_2 enriched	8-14
Mitsubishi	10
WORCA	10
TBRC (Top Blown Rotary Converter)	10-50
Converters	
Peirce-Smith	3-9
Hoboken	10

reasonably even concentration of SO_2 for a conventional acid plant. In plants where flash smelting is also used, it is possible to blend the converter gas to provide a suitable feed for a conventional acid plant. In cases where the SO_2 is treated in an acid plant, the particulate removal will be similar to that of roasting. If the SO_2 is not recovered, high efficiency electrostatic precipitators are normally used to remove the particulate. The converter and the molten metal transfer to and from the converter constitute the greatest fugitive emissions problem in a smelter. Fugitive emissions problems can be reduced by improving the hooding at the converter, sometimes by the use of water-cooled hoods, auxiliary hooding where feasible for converters and metal transfer stations, careful attention to maintenance and operating practices, etc. Where auxiliary hooding is used, particulate removal is usually accomplished with fabric filters.

4.2.4 Continuous Smelting. The control of emissions from the continuous smelter is similar to that from the flash smelter.

4.3 Control Technology. Selection of appropriate techniques for gas purification depends mainly on the substances, concentrations, temperature and quantity of emissions. Components of the gas are (24, p. 509):

- primary dust (i.e., mechanically carried particles of fine to coarser grain size);
- fume (formed by substances that have vaporized and which solidify on entering the dust removal plant. The sizes of the particles vary between 0.01 and 2 μm (predominantly lead and zinc compounds));
- volatile substances (these substances, e.g. arsenic and selenium compounds and mercury are still gaseous on entering the dust removal plant but condense between 50 and 300°C);
- gases such as sulphur dioxide, hydrogen chloride and hydrogen fluoride.

Emissions from roasting, smelting, and converting plants are purified in two phases:

- dust removal by dry purification processes, usually electrostatic precipitators;
- reaction of the gaseous substances in the effluent gases - mainly SO_2 -by means of wet chemical purification processes.

Purification problems, especially in regard to conventional processes, are manifold due to the different characteristics of the effluent gases. Therefore, various solutions have been developed in practical operation. In the following sections, control techniques are described.

4.3.1 **Dust Removal.** The hot effluent gases are cooled in heat exchangers to approximately 200 to 300°C before entering the dust removal plants. Coarse particles of flue dust settle and are withdrawn from the bottom of the heat exchangers or boilers. Cyclones and simple dust chambers are often used to collect the coarse dusts. Electrostatic precipitators are employed for hot, dry, or cold, wet gases.

Fabric filters have dust removal efficiencies of up to 99.9%. Depending on operating conditions, the filtering material consists of natural, synthetic, or glass fibres.

The collection efficiencies of various types of dust removal equipment used in the copper industry are shown in Table 15.

Because of the high content of dust, emissions from roasting are removed by means of either cyclones connected in series or multicyclones followed by electrostatic precipitators.

Flue dust from reverberatory furnaces is recovered by employing electrostatic filters after previous cooling in heat exchangers or boilers. Compared to reverberatory furnaces, charging of fine dry ore concentrates in the flash furnace results in 5 to 10 times higher contents of flue dust. Collection of coarse primary dusts may take place using cyclones (22). Electrostatic precipitators are used to remove the balance of the particulate.

TABLE 15 NEW DUST REMOVAL EQUIPMENT EFFICIENCIES

Dust Collection System	Total Removal Efficiency in %	Pressure Drop (mm H_2O)	Application
High-grade cyclones (Multiple cyclones)	up to 70	50 to 100	Dusts with small fraction under 10 microns
Electrostatic precipitator	up to 99 +	5 to 15	All cases
Combined plant (Electrostatic precipitator with cyclone)	up to 99 +	65 to 100	In special cases with very high dust load and large differences in particle size
Fabric filter	up to 99.9	40 to 100	All cases

Dust is removed from converter gases by electrostatic precipitators or fabric filters.

Dryer gases with a low SO_2 content and substantial flue dust concentrations (approximately 100 g/Nm^3) are initially cleaned in cyclones. Fabric filters or electrostatic precipitators are used to further reduce the particulate content. As an alternative to electrostatic precipitators, wet scrubbers are also used in the copper-making industry.

4.3.2 SO_2 Recovery by Conversion to Sulphuric Acid. Sulphuric acid is the most common sulphur product recovered from metallurgical gases (45). There are fewer restrictions on the characteristics of gases from which acid can be made than in the case of other products, and sulphuric acid is the commonest from in which industry consumes sulphur. Its main disadvantage is that it is expensive both to store and to transport over long distances (45).

In the conventional contact process for making sulphuric acid, a gas containing SO_2 and oxygen in the form of air is heated to a suitable ignition temperature and passed through beds of vanadium pentoxide catalyst. The SO_2 is converted to SO_3 which, when combined with water, produces sulphuric acid. The reaction generates heat which is applied to the incoming gas by means of heat exchangers. Figure 18 shows a single and double contact sulphuric acid plant schematic.

A continuously flowing gas containing 5 - 8% SO_2 and 30 - 50% more oxygen than SO_2 is normal for a conventional contact plant. A gas with intermittent flow or weak in SO_2 requires specially designed oversize heat exchangers and, in some cases, extra heat from external sources. Furthermore, the acid plant must be designed for the maximum or peak flow rate, and thus, intermittent gas flow requires a larger plant for a given daily acid production.

It is essential that gases be thoroughly cleaned before entering the acid plant because dust will choke the catalyst beds and impurities will poison the catalyst and contaminate the acid. Impurities such as selenium and mercury make the acid unsuitable for applications such as fertilizer manufacture. In this respect, gases from metallurgical plants are far more difficult and expensive to deal with than those from sulphur burners.

With normal operation the catalyst deteriorates over time, and the acid plant must be shut down for catalyst screening or replacement. As the catalyst deteriorates, conversion efficiency drops and the SO_2 content of the tail gas increases. When the tail gas emissions increase by 30% above normal, the catalyst is replaced; however, in a

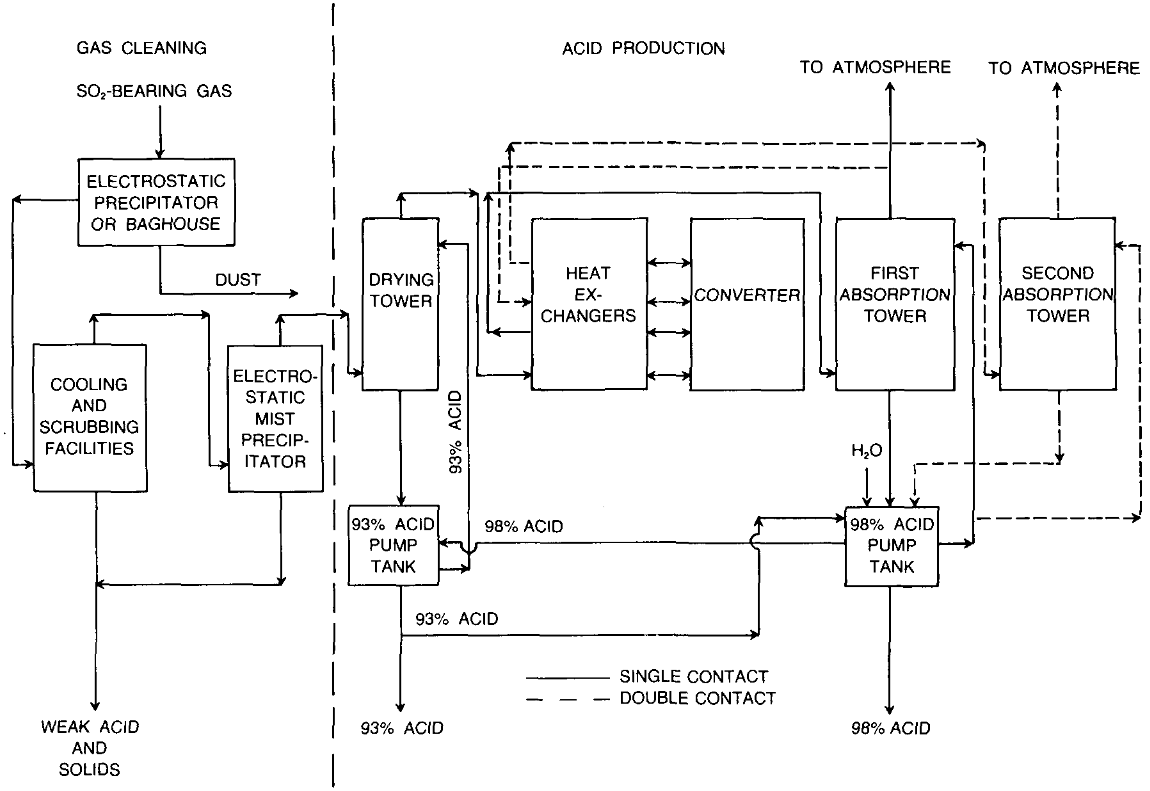


FIGURE 18 SINGLE AND DOUBLE CONTACT SULPHURIC ACID PLANT SCHEMATIC (71)

metallurgical operation the acid plant shutdown is usually scheduled to coincide with such events as the annual boiler inspection or deriming of the oxygen plant.

The gas leaving the absorption tower contains sulphuric acid mist which has to be removed by electrostatic precipitators. It also contains up to 0.2% SO_2 if the single contact method has been used and up to 0.1% when using double contact plants. In a few cases, based on local conditions, the SO_2 content has been further reduced by a tail gas scrubber.

Exit gases with a low SO_2 content can be upgraded by the use of chemical absorption processes.

The remaining SO_2 contents in the cleaned gas differ according to the various processes of sulphur recovery. Operational data for sulphur recovery processes and maximum sulphur dioxide emissions are presented in Table 16. Table 17 summarizes the SO_2 emission control practices in Japan.

4.3.3 SO_2 Recovery by Reduction to Elemental Sulphur (45). From the point of view of shipment or storage, elemental sulphur is the most desirable product since it can be economically transported to much greater distances than either sulphuric acid or liquid SO_2 and can be easily stockpiled when no market is available. However, it is usually the most difficult and expensive of the three to produce.

For reduction of SO_2 in smelter gas to elemental sulphur, it is desirable not only to have a high SO_2 content but also the lowest possible oxygen content, since oxygen increases the consumption of reducing agent.

Sulphur dioxide in smelter gas can be reduced by passing the gas stream through an incandescent coke bed. Processes of this type were operated by Boliden in Sweden, Cominco in Canada, and Orkla in Norway, but all of these plants have now been dismantled because increasing coke costs made them uneconomical.

It is also possible to reduce SO_2 with hydrocarbons such as natural gas, fuel oil, or pulverized coal, all of which are much cheaper reducing agents than coke. Such processes have been investigated since the 1930s and these efforts have recently gathered new impetus. Research work has been carried out by the American Smelting and Refining Company, Texas Gulf Sulphur Company, Outokumu Oy (8), Allied Chemical Company (9) and probably others. American Smelting and Refining and Texas Gulf Sulphur are known to have operated large pilot plants for a considerable time but no commercial process resulted. The only commercial plants were operated by Outokumpu Oy in Finland and

TABLE 16 PRODUCTION DATA AND MAXIMUM SULPHUR DIOXIDE EMISSIONS FOR SULPHURIC ACID PROCESSES

Sulphuric acid recovery process	SO_2 removal	SO_2 concentration in input gas (vol. %)	Maximum sulphur dioxide emissions in gas after treatment
Single contact process	97.5	7 %	5.7 g SO_2/Nm^3
	97.5	6 %	4.8 g SO_2/Nm^3 17 kg SO_2/t H_2SO_4
Double contact process	99.5 %	10 %	1.7 g SO_2/Nm^3 3.3 kg SO_2/t H_2SO_4
	99.5 %	6 %	1.0 g SO_2/Nm^3 3.3 g SO_2/t H_2SO_4
	99.0 %	10 %	3.5 g SO_2/Nm^3 6.6 kg SO_2/t H_2SO_4
	99.0 %	6 %	1.9 g SO_2/Nm^3 5.5 kg SO_2/t H_2SO_4

TABLE 17 COPPER SMELTING TECHNOLOGY AND SO_2 EMISSION CONTROL PRACTICE IN JAPAN

Smelter	1,000 tonnes per year	Smelting process	Off-gas SO_2 %	Furnace gas treatment	Acid plant tail gas scrubber	Sulphur capture, %
Ashio: Furukawa Mining Co.	40	Flash furnace	-	ST acid plant	-	91
		P-S converters	(1)	-	-	
Hitachi: Nippon Smelting Co.	150	Flash furnace, O_2 enriched	10 - 12	DT acid plant	None	97
		P-S converters	4 - 6	ST acid plant	do	
Kosaka: Dowa Mining Co.	60	Flash furnace	8 - 10	do	CaO slurry	99
		P-S converters	4 -6	do	do	
Naoshima: Mitsubishi Metals Co. (2 systems).	150	Fluid-bed roaster	11	DT acid plant	None	98
		Reverberatory furnace	(2)	-	-	
		P-S converters	(3)	-	-	
	50	3-furnace continuous	10	ST acid plant	CaO slurry	
Onahama: Onahama Smelting & Refining Co.	240	Furnace Reverberatory furnace	2 - 2.5	1/2 to MgO scrubber, then strong SO_2 to DT acid plant, 1/2 to CaO scrubber		99
		P-S converters	7 - 9	ST acid plant	CaO slurry	
Saganoseki: Nippon Mining Co.	150	Flash furnace O_2 enriched	10 - 12	DT acid plant	None	97
				ST acid plant	NaOH solution	
		P-S converters	4 - 6			
Tamano: Hibi Kyodo Smelting Co.	80	Flash furnace	7 - 8	DT acid plant	None	99
		P-S converters	(1)			
Toyo: Sumitomo Metal Mining	120	Flash furnace	7-8	ST acid plant	NaOH solution	99
		P-S converters	(1)			

ST = Single train
DT = Double train P-S = Peirce-Smith
1) Combined with flash furnace gas
2) Combined with continuous furnace gas
3) Combined with roaster gas

Bamangwato Concessions in Botswana. Allied Chemical operated such a plant for a short time near Falconbridge, but it was shut down for economic reasons. Phelps-Dodge originally planned to recover elemental sulphur at its new Hidalgo Smelter, and actually built the plant. However, it was never put into operation owing to the high cost of the reductant. Allied Chemical did not reactivate its Falconbridge plant, as part of its recent smelter modification, for the same reasons.

Conversion to elemental sulphur is not complete and other compounds are formed through side reactions. The tail gas thus contains hydrogen sulphide (H_2S) and carbon oxy-sulphide (COS) besides some unreacted SO_2. It is, therefore, necessary to pass the gas mixture through additional catalyst beds at a lower temperature. In these catalyst beds the above-mentioned compounds are reacted with the remaining SO_2. This increases the overall sulphur yield and removes most of such hazardous compounds as H_2S and COS.

As this brief description indicates, reduction of SO_2 to elemental sulphur is a complicated process if objectionable impurities are to be minimized in the tail gas. Even very low concentrations of H_2S and COS are highly objectionable from an air pollution viewpoint. Emission problems can be reduced by oxidizing these compounds to SO_2 in an incinerator before discharging the tail gas into the atmosphere, but only at the cost of additional fuel.

4.3.4 SO_2 Recovery as Liquid Sulphur Dioxide. Sulphur recovery in the form of liquid SO_2 is only practical where a large market (such as paper mills) exists nearby (45) for large quantities of the product.

Gas with the highest possible SO_2 content is desirable for sulphur recovery in the form of liquid SO_2, and it must flow at a steady rate.

There are two main types of liquid SO_2 recovery processes:

Physical recovery process (such as pressure absorption in water and dry compression-refrigeration): The SO_2 content of the gas is the prime economic factor since the gas has to be compressed. In practice, roaster and flash furnace gases are suitable for economic processing by water pressure absorption, as done by the Boliden Company in Sweden. Oxygen flash smelting gas can be economically processed directly by dry compression and refrigeration, as done at Copper Cliff on 80% SO_2 gas supplied by Inco Metals Company from its oxygen flash smelting operation for copper (63).

An important consideration in connection with these physical processes is that the clean gas must be thoroughly dried before compressing and refrigeration. The only practical and economical drying agent for this purpose is concentrated sulphuric acid. For this reason, it is highly desirable to combine liquid SO_2 production by physical recovery processes with a sulphuric acid plant. In such a combination, the moisture in the smelter gas provides the dilution water for the sulphuric acid plant, while the tail gas from the liquid SO_2 plant is processed in the acid plant.

Chemical absorption processes: These are operated at atmospheric pressure and require chemical absorption for SO_2 extraction from the gas stream (45). There are several such processes, but the two best known are the Cominco and the DMA (dimethyl aniline) processes. The Cominco process, developed and employed at Trail, B.C., uses a solution of ammonium bisulphite as the absorbent and strips the SO_2 as a strong (25% SO_2) gas by acidifying with sulphuric acid. Ammonium sulphate is a by-product.

The DMA process was developed by the American Smelting and Refining Company. It was used at the Selby lead smelter in California and is still used by City Service Company in Tennessee, Austriana de Zinc in Spain, and at the Falconbridge nickel refinery in Norway. The most recent installation was at the Asarco copper smelter in Tacoma, Washington (64). In this process, DMA is the absorbent and steam is used to strip the sulphur-strong gas which must then be compressed and refrigerated to make liquid SO_2. The German sulphidine process is very similar. In England, a somewhat different process using basic aluminum sulphate as the absorbent has been developed by Imperial Chemical Industries.

Chemical absorption processes are considerably more expensive than physical recovery processes with respect to both capital and operating costs, but they have the advantage of being applicable to gases with comparatively low SO_2 content, and giving much higher extraction yields than the physical processes. Thus, it is quite possible to extract 98% by chemical absorption processes, whereas it is only economically feasible to extract 90% by physical recovery processes.

4.3.5 Other Sulphur Fixation Processes (1).

- The Citrate process developed by the U.S. Bureau of Mines produces elemental sulphur. A pilot plant has been operated.
- The Asarco Brimstone method which produces elemental sulphur.
- The TGS method for elemental sulphur developed by the Texas Gulf Sulphur Co.

- The double alkali process which produces a throw-away sludge. This has been used at the San Manuel smelting plant in Arizona and more recently at the Afton smelter in Canada (a unique smelter with a low sulphur concentrate).
- The magnesium oxide process is used at the Onahama smelter in Japan to concentrate the SO_2 from a reverberatory furnace for sulphuric acid production.
- The lime-gypsum process is also used at the Onahama smelter in Japan to recover SO_2 from a reverberatory furnace and to produce a commercial gypsum product.

4.3.6 **Arsenic Removal.** The removal of arsenic during copper smelting takes place primarily by two mechanisms: volatilization and slagging. The distribution of arsenic among the materials discharged will vary according to the process. In the presence of oxygen, elemental arsenic or arsenic sulphide oxidize to As_2O_3 which is extremely volatile. However, in an oxidizing atmosphere, the arsenic trioxide may oxidize to the higher oxide As_2O_5 which is less volatile and forms stable non-volatile arsenates with other metallic oxides.

When As_2O_3 is produced, the exit gases must be cooled to condense the arsenic trioxide to the solid form before the gases undergo particulate removal.

Under the oxidizing conditions required for sulphur removal in the roasting of copper concentrates, As_2O_5 is usually formed. This compound may react with calcium or iron to form stable and non-volatile arsenates which remain in the calcine. The arsenic compound would then report to the slag and matte in the subsequent smelting operation (depending again upon the smelting atmosphere) and as particulate in the exit gases.

Arsenic Behaviour in Metallurgical Processes:

Roasting.

In special cases, when sulphide concentrates are roasted, as much as 95% of the contained arsenic may be driven off in the gases. More typically however, with low levels of arsenic in the feed, up to 50% will be volatilized initially and most of this will be recycled with the flue dust and become fixed in the calcine (46).

Reverberatory Smelting.

Of the arsenic in partly roasted new charge to a reverberatory or electric furnace, 20 to 50% will leave in the gas phase and somewhat more in the case of uncalcined concentrates. Most of this arsenic will be recycled with flue dusts and end up in the matte and, to a lesser extent, in the slag (46).

Flash Smelting.

This process combines roasting and smelting in one furnace. Up to 75% of the new input arsenic is volatilized and, as in the other processes, most of it is usually recycled in flue dusts, although a hot-cold dust separation can be used to remove arsenic from the circuit (46).

Converting.

In a conventional batch converter, the amount of arsenic carried off in the gases depends largely on the grade of the matte. In the case of a high grade matte, metallic copper appears early in the converting cycle and acts as a collector of arsenic so that 20% or even less of the arsenic may be volatilized, while with a low grade matte, up to 50% may enter the gases.

Noranda Continuous Copper Smelting Process.

When the Noranda reactor is being operated to make high grade matte, about 85% of the arsenic enters the gas stream. When making copper only about 20% is volatilized, although the use of oxygen enrichment in the converter air increases this to about 40%.

Mitsubishi Continuous Copper Smelting Process.

Data are not yet available for arsenic behaviour in this system, but the smelting furnace probably gives similar results to the Noranda reactor when producing matte; volatilization in the converting furnace should be similar to that in the Noranda reactor when producing copper. The main difference is that smelting and converting are carried out in separate vessels in the Mitsubishi process (46).

Top Blown Rotary Converter.

This process is coming into use for treatment of a great variety of feeds, including nickel and copper sulphide concentrates, nickel laterites, and lead residues. The arsenic behaviour will differ with different feeds but in one reported test with copper concentrates, over 65% of the arsenic reported in the flue dust (46).

Hydrometallurgical Processes.

Arsine gas (AsH_3) can be produced in certain hydrometallurgical processes when nascent hydrogen is evolved in the presence of dissolved arsenic. In the purification of copper refinery electrolyte about 30 - 40% of the arsenic in solution may be reduced to arsine. This is usually a workroom environment problem rather than one of atmospheric pollution. The quantities of arsine are small and normally dealt with by dilution and venting to the atmosphere.

4.3.7 Mercury Removal. Mercury boils at 357°C and has a vapour pressure of 0.001 Hg at 20°C. Consequently, in pyrometallurgical processes it vapourizes early in the process and enters the gas stream.

Most base metal sulphide ores contain some mercury. The amount is usually very small. In Canada, lead and zinc ores generally have a higher mercury content than ores of other base metals and western Canadian ores more than those in the east (69).

Virtually all the mercury in a smelter feed will be volatilized and enter the gas stream. Where mercury levels are high, some of it will condense and be collected in the cooling and cleaning system. However, elemental mercury vapour below saturation level in the cooled gas will not be caught unless the gases are specially treated or go through an acid plant. Roughly half the mercury reaching an acid plant will be collected in the weak acid scrubber and half in the product acid. In some cases, such as in the manufacture of fertilizers, the presence of mercury in the acid renders it unuseable. In such cases, mercury must be removed from the gases before they go through an acid plant, from the acid itself or both.

The gases may be treated by dry absorption in towers containing selenium, activated carbon, or other material; by wet scrubbing with concentrated sulphuric acid, a selenium suspension, or chloride solution; or by injection of hydrogen sulphide into the gas stream. Simple cooling may also be used but mercury below saturation levels in the cooled gas will not be extracted.

Processes have been developed for removing mercury from sulphuric acid as a filterable precipitate by addition of sulphur, iodides or aluminum (69).

5 CANADIAN COPPER PRODUCING OPERATIONS

5.1 Noranda Mines Ltd., Horne Division

The Noranda smelter has two wet-charge reverberatory furnaces, a Noranda continuous process reactor and five Peirce-Smith converters. Off gases from these units are treated in electrostatic precipitators for particulate removal and vented to the atmosphere through 2 stacks, 160 metres and 129 metres tall respectively. Figure 19 shows a smelter flow sheet.

A 450 tonne per day oxygen plant is currently under construction. This will be used to increase productivity in one reverberatory furnace and the Noranda Process Reactor, and allow the shutdown of one reverberatory furnace.

The original smelter, consisting of two hot-charge reverberatory furnaces, eight multi-hearth roasters and two converters, was built in 1927 to treat the output of the Horne mine. As the production of the mine decreased, the smelting of custom concentrate increased. Since the closure of the mine in 1976, the smelter has been solely a custom smelter.

The Noranda continuous smelting process (33) has been in operation since 1973. A description of the Noranda process was given in Section 2.2.14. Table 18 shows principal operating data for three years, 1977-79.

Although the heat required to supplement that generated by the exothermic smelting reactions in the reactor can be provided either by gas, oil, or solid fuel, singly or in a variety of combinations, it has been found most effective to add the fuel to the reactor bath. It is then burned in contact with the charge, using the tuyere air to supply the oxygen for combustion. Approximately 30% of the fuel requirement is provided by Bunker 'C' oil which is introduced into the furnace from a 0.635 cm diameter nozzle located in the feedport. No attempt is made to atomize the oil which flows as a continuous jet onto the bath surface. Off-gas analysis shows that complete combustion takes place.

The major part of the fuel requirement is supplied by solid fuel which is introduced into the furnace with the feed.

5.2 Noranda Mines Ltd., Gaspé Division

The original smelter, comprised of a reverberatory furnace, Peirce-Smith converters and anode furnaces, was brought into operation in 1955. A major modernization of the plant was completed in 1973-74. A fluid bed roaster and an acid plant were

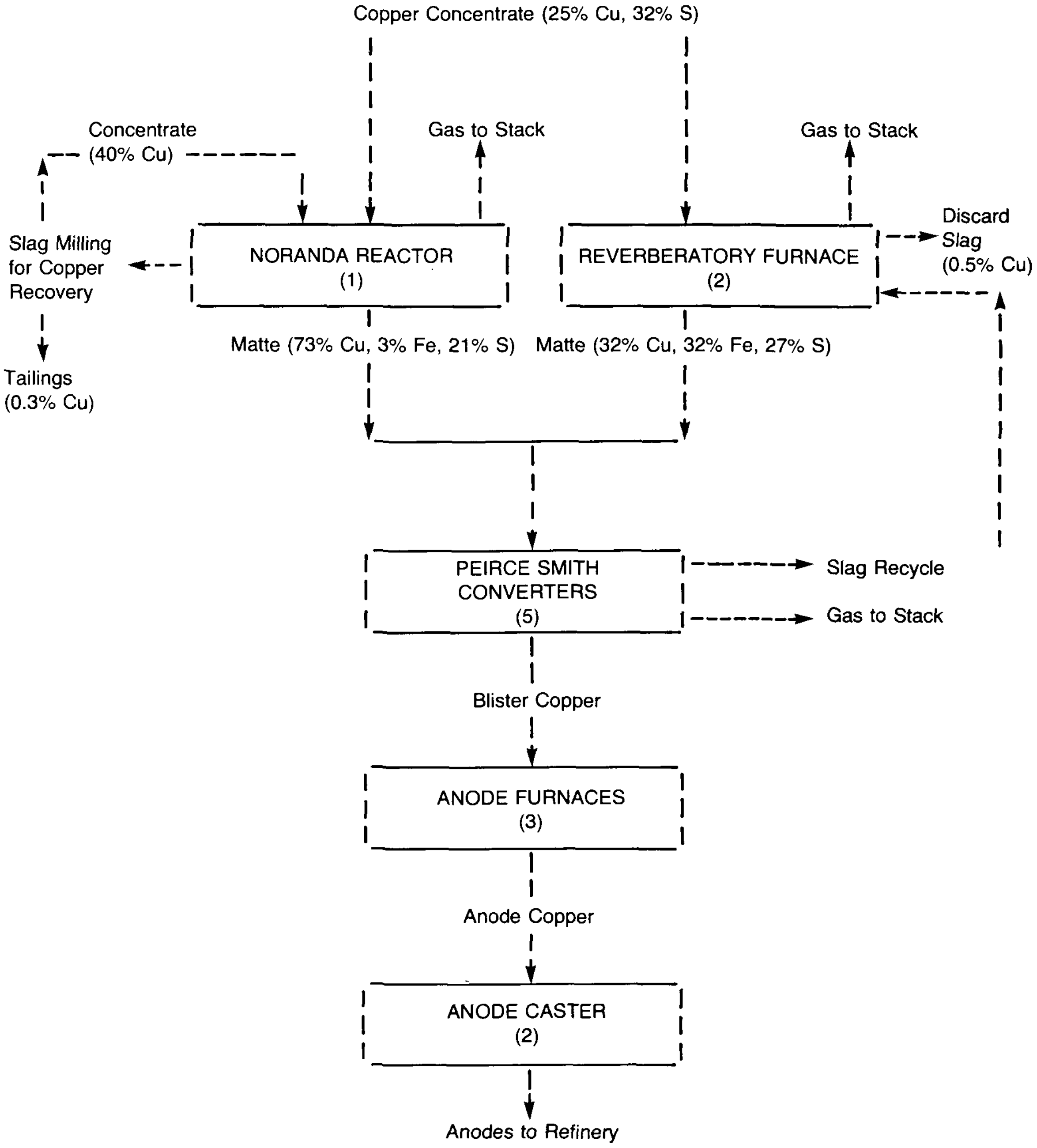


FIGURE 19 NORANDA SMELTER FLOW SHEET AS OF JANUARY 1980

TABLE 18 PRODUCTION DATA - NORANDA PROCESS REACTOR 1977-79 (33)

Campaign No.	17	18	19	20	21	Average
Campaign Days	180	165	211	201	160	180
% Blowing Time	86.3	87.1	91.1	89.1	83.0	87
Average Blowing Rate, SCFM	41,126	41,513	41,240	38,811	41,579	41,000
Instantaneous Smelting rate, SDT*/Day	1,184	1,194	1,251	1,240	1,206	1,215
Fuel Ratio, MM Btu/SDT Cu Conc.	2.76	2.20	2.39	2.70	2.83	2.57
Slag Tailings, % Cu	0.35	0.35	0.35	0.30	0.27	0.32
Brick Consumption - Lbs. Ref. Replaced/ SDT Cu Conc. Smelted	2.04	0.61	0.69	0.61	2.12	1.22

* Short dry tons

constructed and started up in 1974. At present, the Gaspé Smelter consists of a fluid bed roaster, a reverberatory furnace, two Peirce-Smith converters, one rotary anode furnace and a sulphuric acid plant. Figure 20 shows a smelter flow sheet.

The Gaspé Smelter acid plant treats both roaster and converter off gases. The particulates from the reverberatory furnace gas are removed in an electrostatic precipitator. The reverberatory furnace gas is then emitted, along with the acid plant tail gas, into the atmosphere through a 152 metre stack.

Two-thirds of the feed to the smelter is provided by concentrate produced by the Gaspé Division and one-third by custom concentrates originating from mines located in Quebec and the Atlantic Provinces.

5.3 Inco Metals Co. Ltd., Copper Cliff, Ont.

Inco mines 15 million tonnes/year of nickel/copper ore from several mines in the Sudbury district. The ore is treated in the company's concentrator to produce 1.5 million tonnes of nickel concentrates and 0.5 million tonnes of copper concentrates per year. Both concentrates are smelted and converted in the Copper Cliff smelter which has

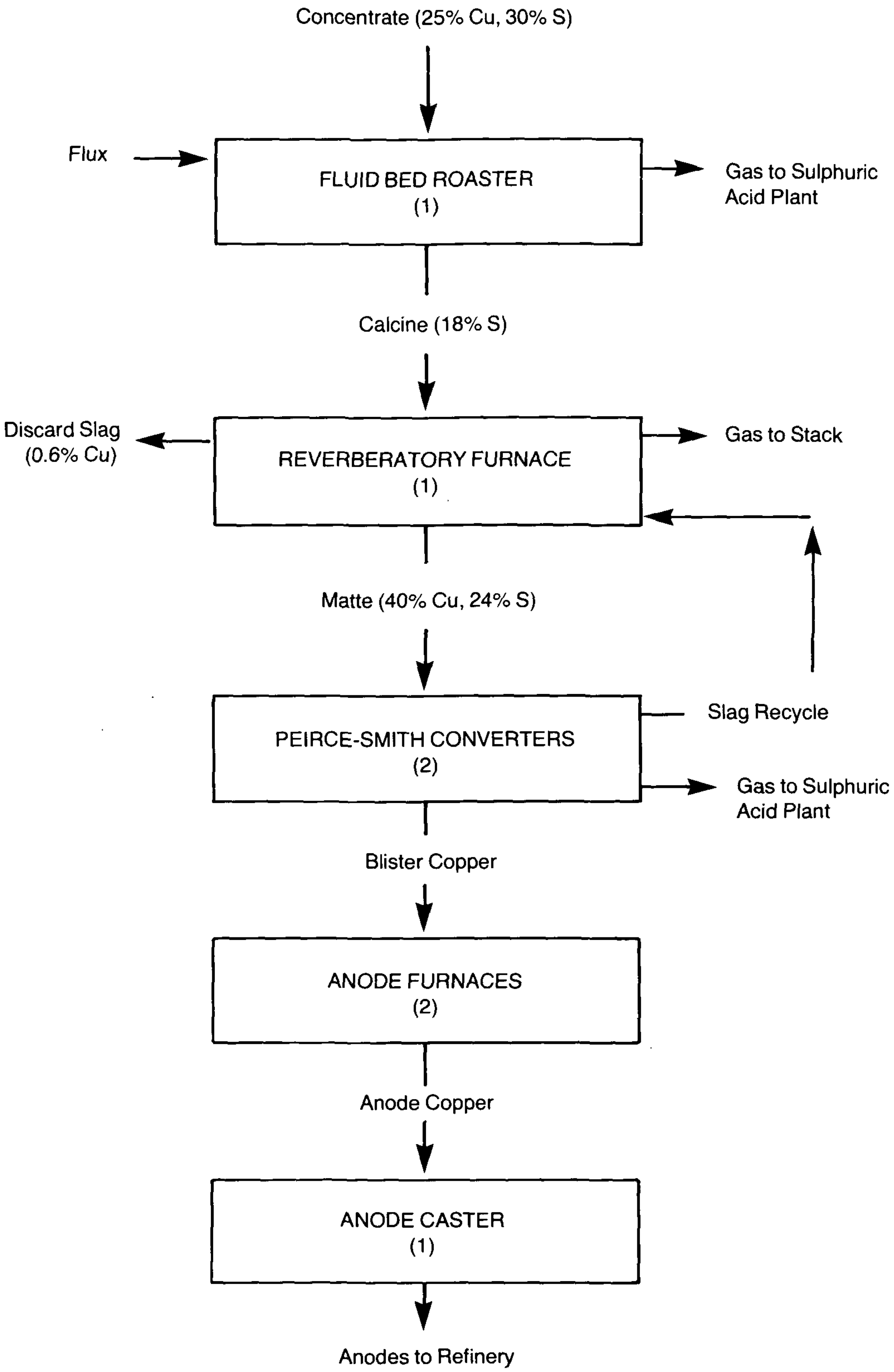


FIGURE 20 NORANDA MINES, GASPÉ DIVISION COPPER SMELTER FLOW SHEET

both nickel and copper circuits. A simplified flow sheet is shown in Figure 21. Details of the nickel circuit are available in the literature (35, 36).

THE COPPER CIRCUIT (34)

Drying

The copper concentrate, containing 30% Cu, 33% S and 1.2% Ni and averaging 80% minus 75 microns (200 mesh), is received at the dryers in the form of filter cake containing 8-9% moisture. It is mixed with 8-10 weight percent sand, averaging 60% plus 210 microns (65 mesh) and 3-5% moisture. The mixture is dried in two drying lines, each consisting of a blower, fluidizing air preheater, fluidized bed dryer and a product collection baghouse. The capacity of each line is 900 TPD of concentrate. Each fluid bed dryer consists of:

- a refractory lined windbox at the base of the unit;
- a refractory grate containing tuyeres;
- a refractory lined fluid bed shaft.

The dryers are approximately 2.7 metres in diameter with 1.5 metre beds and 2.9 metre freeboards.

The fluidizing air is preheated in a horizontal, refractory lined combustion chamber fired by natural gas or light industrial oil. The wet concentrate-flux mixture is introduced to the dryer through a rotary sealing feeder of Inco design. The particles are suspended in the upward stream of hot gases coming from the preheater; all the water is evaporated. The moist gases and dry solids are drawn out through the dryer roof for separation in a baghouse. Normal operating conditions at Copper Cliff are:

- a windbox temperature of about 315°C;
- a bed temperature of about 120°C;
- a gas and product exit temperature of about 105°C.

Heat balances indicate that about 60% of the heat input is used for moisture elimination, about 10% is contained in the dry product, about 25% in the waste gases, and about 5% is assigned to heat losses.

The baghouses operate at a collection efficiency in excess of 99.9%. A system of screw conveyors discharges the dried feed from the hoppers located at the bottom of the baghouses and transfers it to the furnace feed bins.

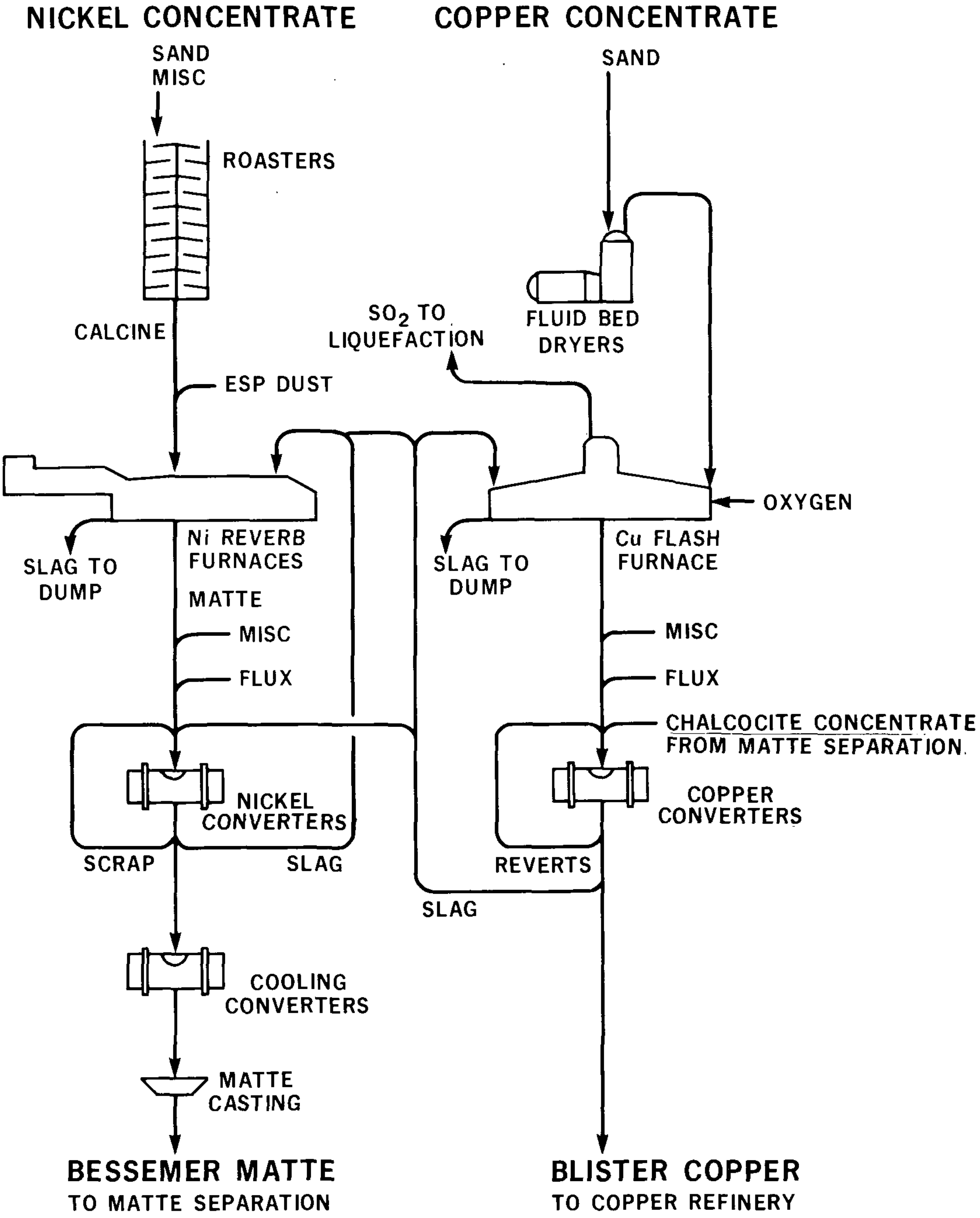


FIGURE 21 COPPER CLIFF SMELTER FLOW SHEET (37)

Flash Smelting (34)

A cutaway view of the flash furnace is shown in Figure 10. The furnace, of a very simple design, is contained in a welded mild steel shell, except for openings on the side walls at the slag level to permit direct air cooling. The outside dimensions of the furnace are: length, 24.4 metres; width, 7.3 metres; and height at the ends, 5.7 metres. The sprung-arch roof and the walls are constructed of chrome-magnesite brick. Approximately 20 percent of the side walls are covered with water-cooled copper jackets in the mid-furnace area. The furnace bottom is of magnesite brick.

The furnace is fired from both ends by four burners, two at each end. Each burner is fed from its own dry feed bin. The solids are withdrawn from the bins at a controlled rate and transferred to the burners by screw conveyors and gravity. Recycled dust and touch-up sand, if required, are added to the screw conveyors also at a controlled rate. The oxygen, at over 96% purity, is supplied from on-site oxygen plants and delivered to the furnace burners at 205 kilopascals (about 2 atmospheres absolute pressure).

The feed is picked up in the horizontally flowing oxygen stream and injected into the furnace. The oxygen readily reacts with part of the sulphur and iron in the concentrate to form SO_2 and iron oxides. Silica, contained in the flux and concentrate, combines with the iron oxides to form a slag. Copper, except for a minor amount lost in the slag, and the remaining iron and sulphur, collect in the matte.

The furnace has two matte tapping holes, both located on the same side wall, and one slag skimming hole located at one end of the furnace. Matte is tapped at about 1175°C in 22 tonne quantities and moved by rail transfer-car to the converter aisle. Slag is skimmed at about 1230°C and discarded.

A total of 250-350 MTPD of converter slag is being reverted to the furnace at present. This represents about 50% of the slag generated. The slag is poured from ladles down a 13 metre launder and enters the furnace through an opening in the end of the furnace opposite to that from which the discard furnace slag is skimmed (70).

Gas Cleaning System

The relatively low volume of off gas, about 20% of other processes and containing less than 3% of the dry solid charge as dust, exits the furnace at about 1260°C. The gases are thoroughly cleaned prior to delivery to a SO_2 liquefaction plant. They are passed first through a settling chamber, which collects some of the dust for return to the furnace and also cools the gases to about 700°C. Further cooling is achieved with water in a splash tower. The gases are then passed through three Venturi scrubbers in series and an electrostatic precipitator before being piped to the Inco liquefaction facilities. The underflows from the splash tower and scrubbers are taken to a settling cone: the overflow from the cone is cooled and recycled. The underflow slurry is stripped of SO_2, neutralized with lime and reverted to the concentrator. Gas delivered for liquefaction is shown by analysis to contain 70-80% SO_2. It should be noted that if this off gas were to be delivered to a sulphuric acid plant, the furnace flue system could be greatly simplified by using only a gas conditioner for cooling followed by an electrostatic precipitator.

Copper Converter Slag Disposition

Plant scale testing by the company (37) of copper converter slag recycle to the flash furnace has demonstrated the technical feasibility of slag cleaning to discardable levels at present. About half the converter slag is being handled in this manner, but because of the presence of nickel in the copper concentrate the remaining half of this slag is being reverted to the nickel reverberatory furnaces as a bleed for this nickel contaminant. If nickel were not present full recycle of converter slag to the flash furnace for cleaning could be practised. Figure 22 presents a schematic flow sheet for a hypothetical smelter treating 1200 tonnes/days of copper concentrate (37). The mass balance and energy requirements are shown.

Copper Converting

Converting is carried out in four Peirce-Smith converters. Since the nickel concentrate (fed to the nickel circuit) contains about 25% of the copper input to the smelter and the copper concentrates contain about 3% of the nickel input, converter procedures at Inco differ in some aspects from those at many other copper smelters.

As stated previously, copper converter slags reversion is split about 50/50 between the flash furnace and the nickel reverberatory furnaces. As well, the chalcocite concentrate produced by the copper-nickel matte separation process is smelted and converted in the copper converters. Also, in order to eliminate the nickel that accumulates in the converter from the materials charged, a special finishing procedure is followed. The nickel is removed by oxidation during the finishing blows. The resulting nickel oxide forms a solid crust on top of the blister copper. This crust remains behind in the converter after casting. This is removed by performing a "washout". To accomplish

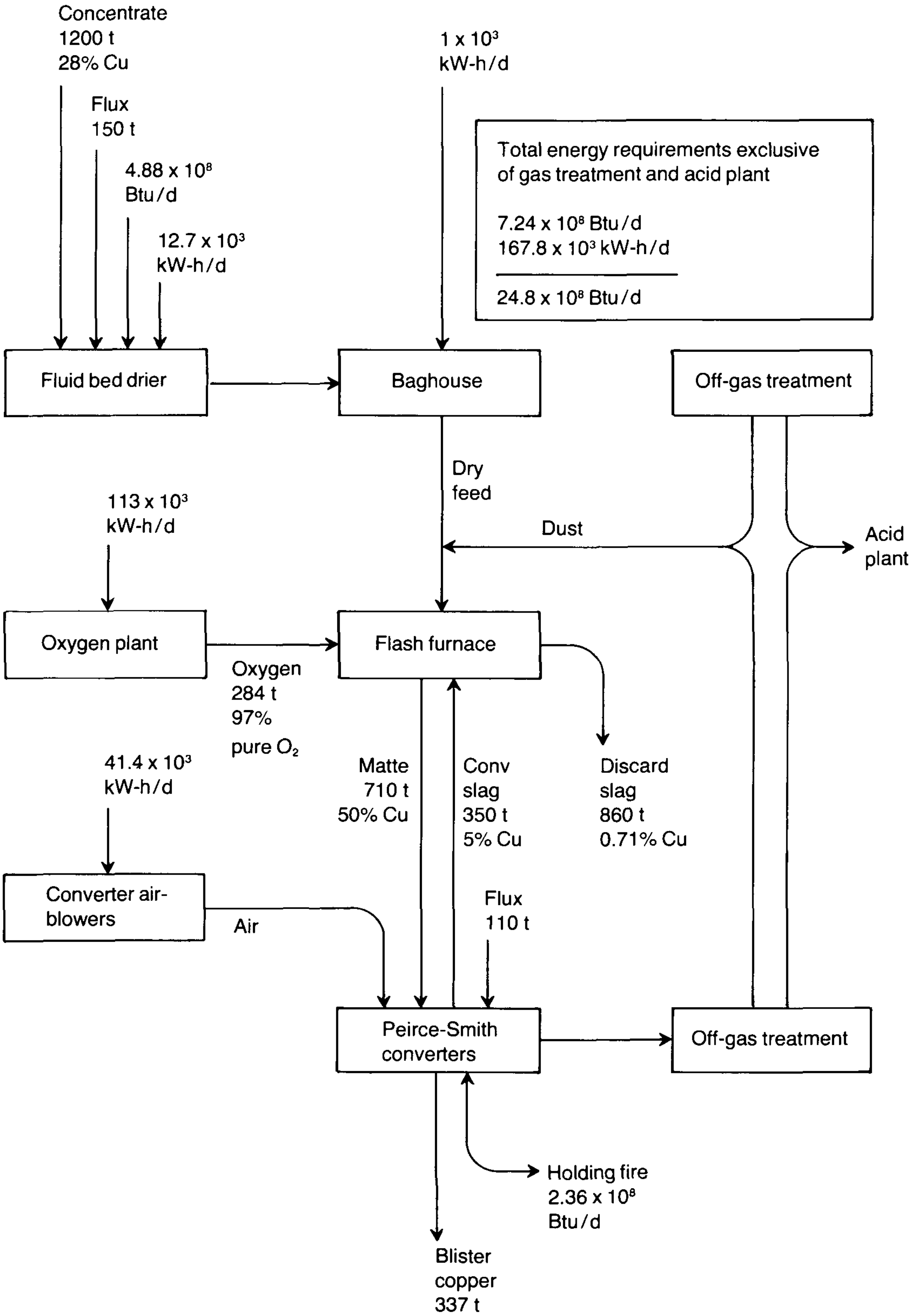


FIGURE 22 SCHEMATIC FLOW SHEET FOR FLASH SMELTING AND CONVERTING A TYPICAL COPPER CONCENTRATE. MASS BALANCE (TONNES/DAY) AND ENERGY REQUIREMENTS (37)

this, the converter is charged with about 80 tonnes of nickel reverberatory furnace matte. About 10 tonnes of flux are added and a short blow is made. The resulting slag and matte are transferred to the nickel converters for treatment.

Oxygen enrichment to an oxygen content of 30 percent in blowing air is used as required (36).

After removal of particulate in an electrostatic precipitator, converter gases are vented to the atmosphere via a common 380 metre stack.

The blister copper is transferred to rail mounted hot metal cars for delivery to the company's nearby electrolytic refinery.

5.4 Falconbridge Nickel Mines Ltd., Falconbridge, Ont.

This company processes a bulk nickel-copper concentrate produced in its mines in the Sudbury district (65).

The concentrate, in slurry form, is partially roasted in fluid bed roasters and the calcine is smelted in electric furnaces. The roaster gases are treated in an acid plant. The electric furnace matte is further treated in Peirce-Smith converters to produce a nickel-copper matte which is shipped to the company's refinery in Norway. There, it undergoes further processing to refined products including nickel, copper, cobalt, sulphur and precious metals. Figure 23 is a flow sheet of the 1980 Falconbridge operations.

5.5 Hudson Bay Mining and Smelting Company Ltd., Flin Flon, Manitoba

The Hudson Bay Mining and Smelting Co. Limited (H.B.M.& S.) operates a copper-zinc metallurgical complex in Flin Flon, Manitoba. Feed to the process is a combination of custom and captive concentrates. Copper is extracted through pyrometallurgical processes, whereas zinc is extracted through a combination of roasting, electrowinning and slag fuming.

Copper Smelter - Zinc plant residue is mixed with the custom and captive copper concentrates, dried in one of two rotary dryers and fed with flux material into five coal-fired multiple hearth roasters. A smelter flow sheet is shown in Figure 24.

Exhaust gases from the rotary dryers are passed through cyclone type dust collectors and then to the atmosphere. The dust collected in the cyclones is recycled to the feed to the roasters.

Exhaust gases from the roasters are passed through an electrostatic precipitator and then to the atmosphere via a 250 metre stack. The dust collected in the electrostatic precipitator is recycled to the reverberatory furnace for processing.

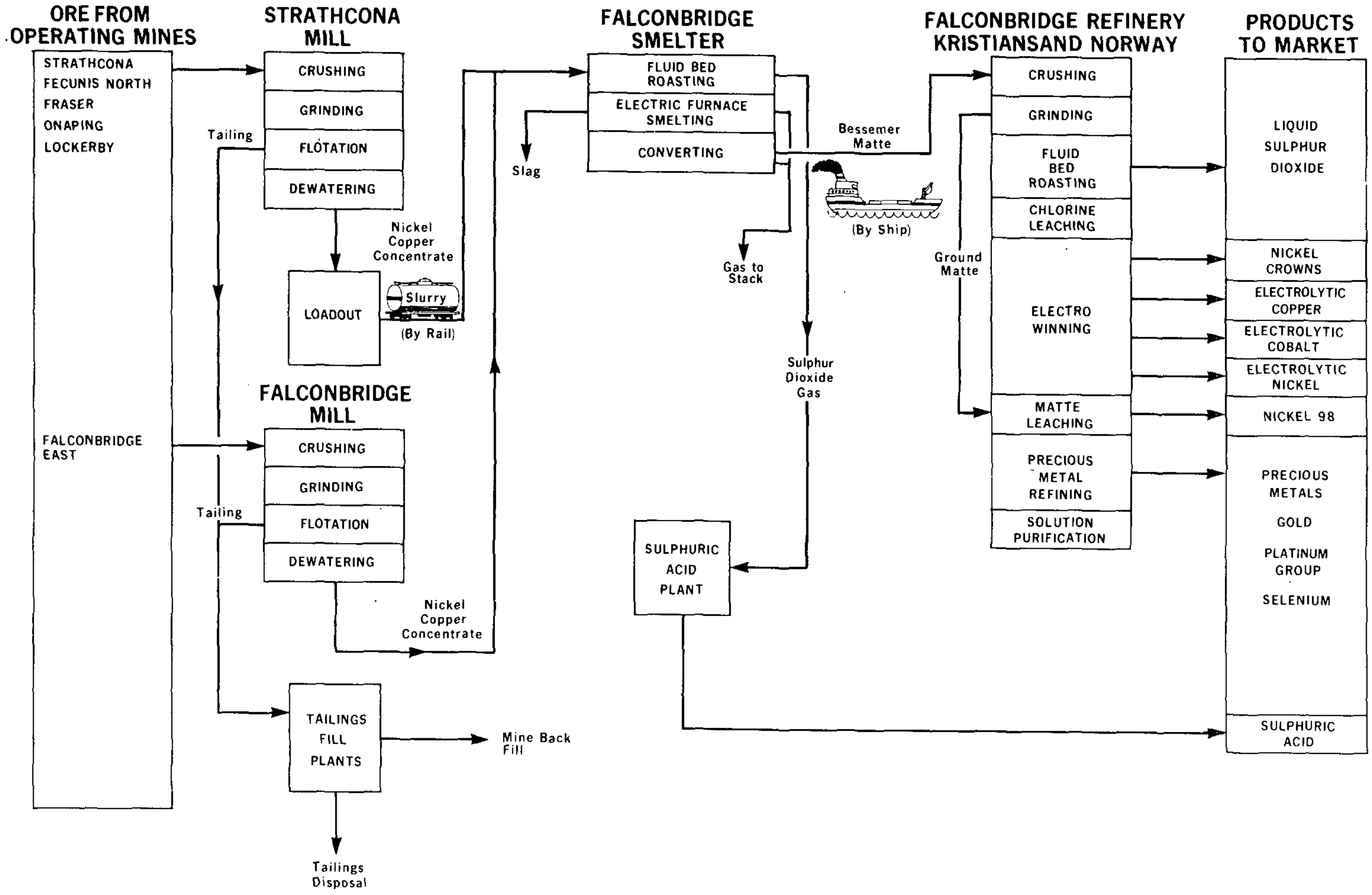


FIGURE 23 FALCONBRIDGE NICKEL MINES LTD. - OPERATIONS FLOW SHEET, 1980

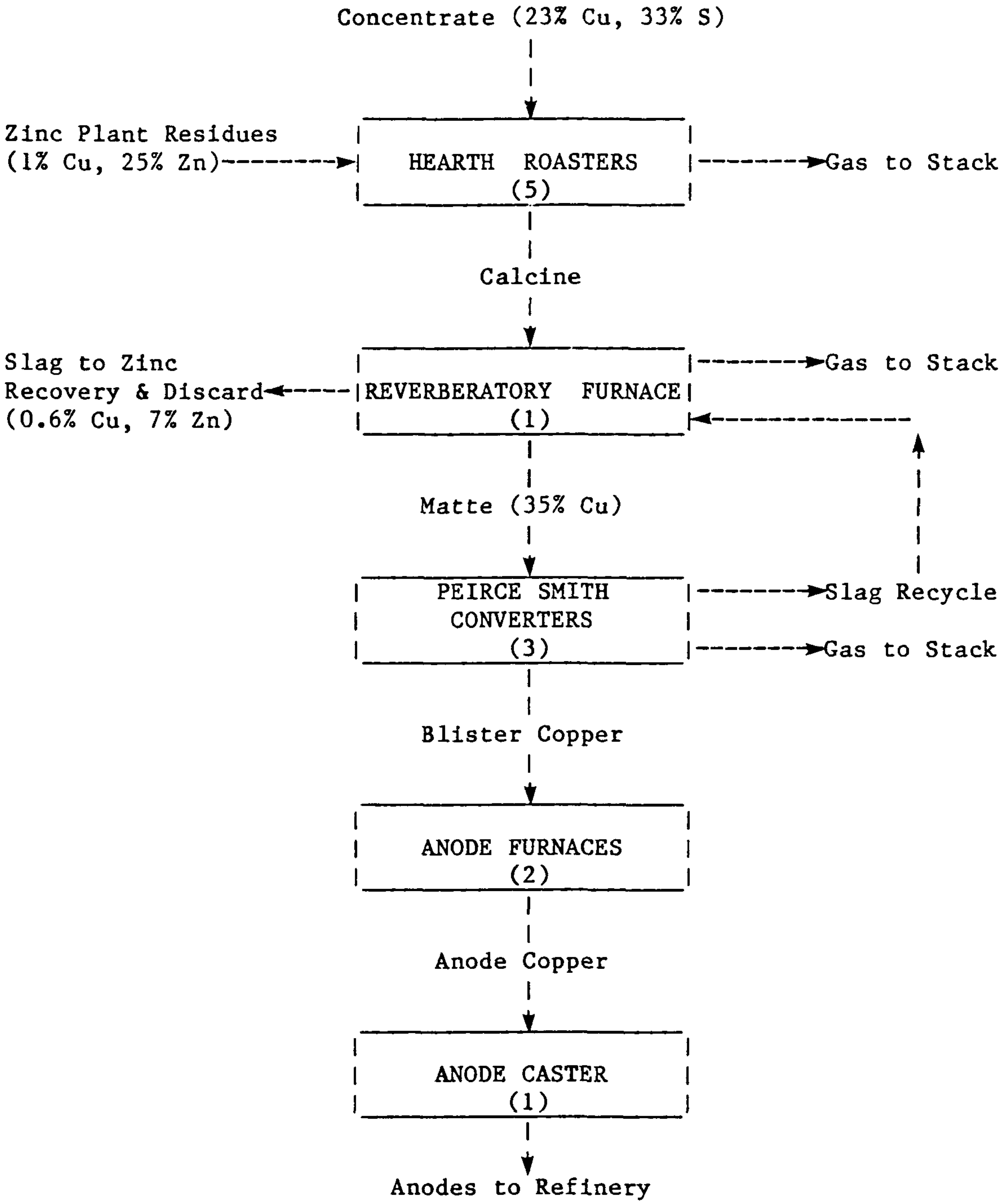


FIGURE 24 SMELTER FLOW SHEET - HUDSON BAY MINING AND SMELTING, FLIN FLON, MANITOBA

The roaster product, containing 12-18% sulphur, 15-19% copper, 25-35% iron, plus silicates and some zinc is fed into an oil-fired reverberatory furnace, where it is melted and separates into two immiscible liquid phases: matte and slag.

The slag is processed in the fuming furnace for zinc recovery. Exhaust gases from the reverberatory furnace are passed through waste heat boilers, an electrostatic precipitator, a fabric filter and then to the atmosphere via the 250 metre stack. The dust collected in the electrostatic precipitator is recycled to the reverberatory furnace for further processing. The dust collected by the fabric filter is recycled to the zinc plant for further processing. The matte from the reverberatory furnace is transferred to three converters. Converter slag is returned to the reverberatory furnace for cleaning. Matte is periodically added and slag skimmed off until there is sufficient copper sulphide in the converter to contain about 41 tonnes of copper. The charge is then blown with air to eliminate the sulphur and produce blister copper.

Exhaust gases from the converter operation are passed through an electrostatic precipitator, a fabric filter and then to the atmosphere via the 250 metre stack (these collectors are common to the reverberatory furnace operation as well).

In addition, due to the nature of the operation of the converter, fugitive emissions of sulphur dioxide and particulate matter result during charging and tapping of the converter. These are discharged directly to the atmosphere via roof ventilators over the converter aisle.

The blister copper is transferred to holding furnaces in the anode casting area for final refining and casting into various anode shapes.

Exhaust gases from the anode casting area which contain a small amount of sulphur dioxide are discharged directly to the atmosphere via roof monitors over the area.

5.6 Afton Mines Ltd., Kamloops, B.C. (39)

The Afton smelter, which commenced operation in 1977, is the first commercial application of the Top Blown Rotary Converter (TBRC) process for the combined smelting and converting of copper concentrates. The single TBRC unit (Figure 8) treats a combined charge of copper gravity concentrate and flotation concentrate in a batch operation. It completes 2 heats per day of 45 tonnes of blister copper (99%) per heat.

The Afton mine and mill have been designed to process 6 400 tonnes of copper ore per day. The orebody is mainly native copper and bornite (Cu_5FeS_4) with chalcocite

(Cu_2S) and chalcopyrite ($CuFeS_2$) in the deeper deposits. The mine itself is located near Kamloops, and is developed as an open-pit operation. Proven ore reserves are estimated at about 31 teragrams (million tonnes) grading 1% copper. Additional copper reserves have also been located in deeper deposits and will likely be recovered in the future by conversion to an underground operation.

The ore is transported to the nearby mill/concentrator complex where it is first crushed and processed to produce two distinct types of copper concentrates to feed the smelter's TBRC. A high-grade metallic concentrate containing coarse native copper flakes is first separated from the sulphide mineralization by a series of screens, shaking tables and jigs. The resulting high gravity concentrate contains about 80-90% copper.

A second, more conventional flotation concentrate is also produced containing about 55-60% copper and 3.5% sulphur, compared with a typical B.C. copper concentrate containing 28% copper and 35% sulphur. The flotation concentrate is thickened, filtered and dried before being introduced into the rotary converter. Figure 25 is a flow sheet of the smelter.

Afton's TBRC is 4.26 metres in diameter and 6.40 metres in length. It is designed to produce blister copper. In the TBRC process, copper flotation concentrate and metallic concentrate are blended with limestone to form a suitable charge. The oxygen/fuel ratio is adjusted while the charge mixture is being fed to the converter through the charging chute. The concentrate mixture is first melted by the oxy-fuel flame which is replaced later by oxygen blowing into the subsequent molten bath through the lance. Because of the rapid oxidation of impurities, the heat losses are relatively small and no external heat is required.

The oxygen lance can be adjusted from a central control room to control both the angle of impingement and the depth of penetration into the vessel. After sufficient slag volume has accumulated in the converter, the concentrate feed and rotation are stopped and the first slag poured into a refractory-lined ladle. Slags that require subsequent cleaning operations to recover metal values are cooled, crushed and processed in the concentrator to recover retained copper phases.

After the first slag is removed, the furnace returns to its operating position and smelting resumes until all concentrate has been charged. Slag volume is allowed to build up once more and is subsequently removed. The resulting white metal (90% Cu) is blown to blister copper (99.6% Cu) which is poured into moulds to cast billets weighing 545 kg for shipment to Britain.

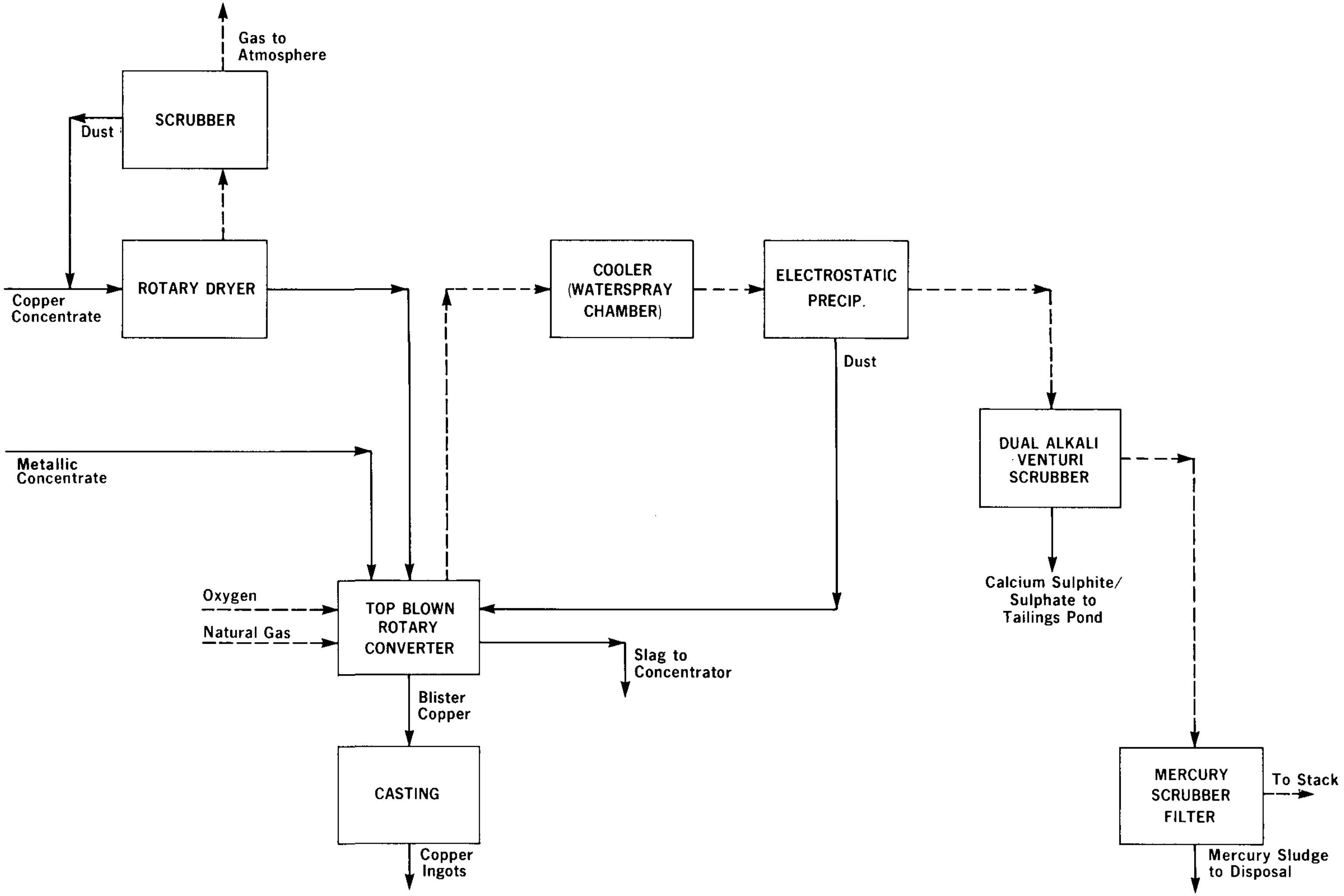


FIGURE 25 FLOW SHEET OF AFTON SMELTER

The Afton smelter generates a low volume of concentrated sulphur dioxide off gas due to the unusually low sulphur content of the feed material. All exhaust gas from the TBRC process is collected and processed in a four-stage dual-alkali scrubbing system.

In the first stage, the process gases are quenched in a waterspray chamber to reduce their temperature from a range of 760-820°C to about 340°C. Particulates in the exhaust gases are removed by an electrostatic precipitator. In the second stage, which is designed to absorb the SO_2 from the gas stream, the gas is contacted in a special tower with a sodium sulphite solution. The third stage cools the gas. This allows for any mercury vapour to condense in the fourth stage (which includes a proprietary filter). Finally, the gas is vented to the atmosphere via a 90-metre tall stack.

Difficulty has been experienced in the operation of the gas scrubbing system and revisions are being considered.

6 COST OF DEVELOPMENT AND OPERATION OF PRIMARY COPPER PRODUCTION PROCESSES WITH EMISSION CONTROL

In many cases, pollution control from existing Canadian sources would require replacement of all or part of existing facilities.

Table 19 shows a capital cost breakdown for a copper smelter/refining complex as represented by the flow sheet in Figure 26 (41). This would be a flow sheet for a plant producing 60 000 - 100 000 tonnes per year of cathode copper and usual by-products (eg. sulphuric acid, precious metal) from copper sulphide concentrates containing 25-30% copper.

TABLE 19 TYPICAL COST BREAKDOWN FOR 100 000 TONNES/ANNUM COPPER SMELTER - REFINERY COMPLEX (MID-1976 COSTS) (41)

Section	Indicative capital cost, SU.S. x 10^{-6}	Indicative production cost, c/kilo
Concentrate handling	9.6	1.92
Matte smelting	30.6	9.22
Slag cleaning	7.8	3.42
Matte conversion	22.2	6.66
Acid plant	13.0	3.86
Anode casting	4.2	1.76
Copper refinery	27.0	6.83
Precious metals refinery	2.6	1.10
Effluent treatment	2.2	1.15
Site utilities	22.0	4.59
Site services	5.2	1.26
Oxygen plant	5.4	2.16
Working capital	15.4	-
Pre-operating expenses	6.8	-
Financing costs	26.0	-
Administration, selling, etc.	-	11.20
	200.0	55.13

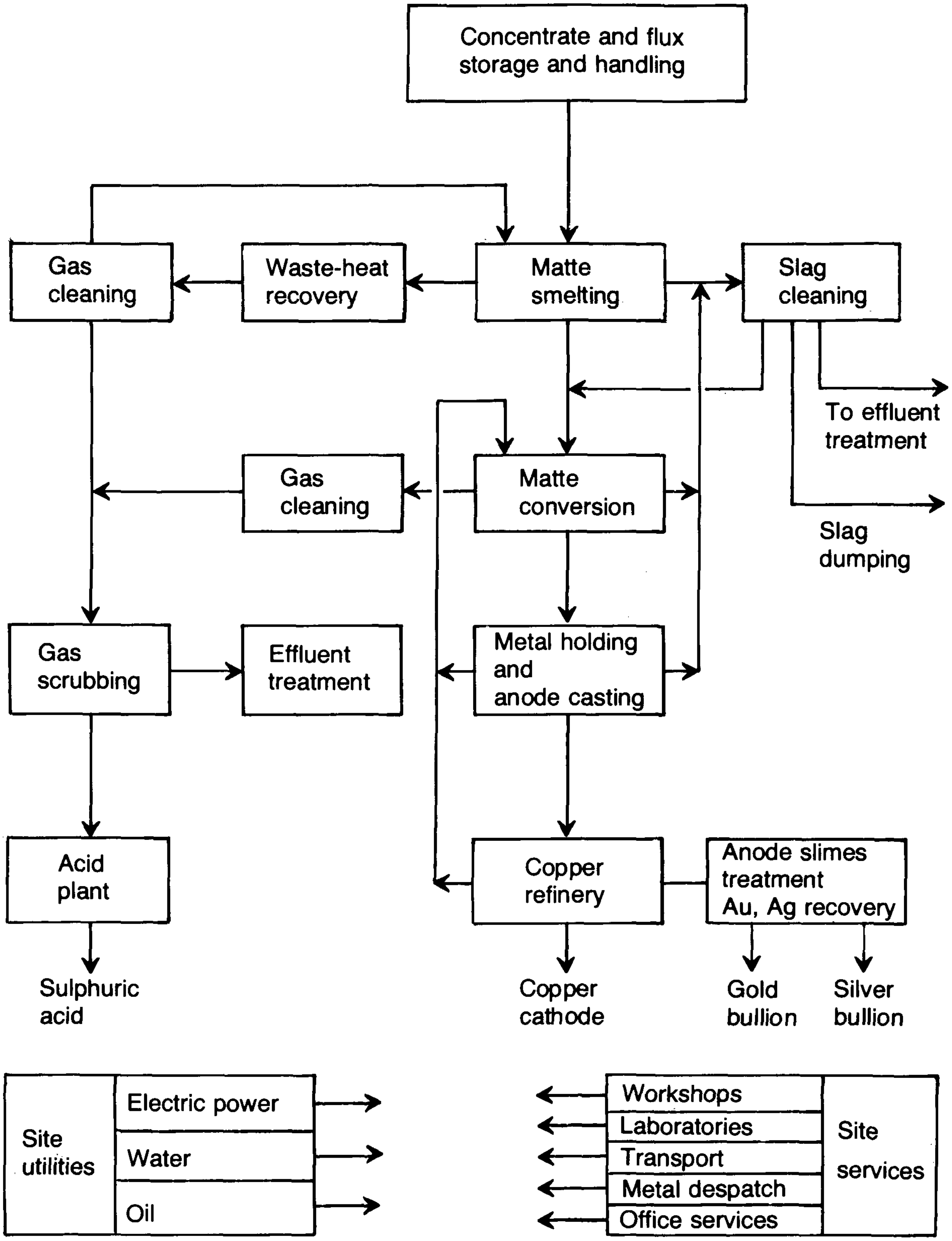


FIGURE 26 COPPER SMELTER - REFINERY FLOW SHEET (41)

Costs are based on design data for a "green-field" site which covers everything within the perimeter fence (including, for example, offices, laboratories and workshops).

As shown in Table 20, which gives a cost analysis by section, the cost of emission control in a given "green-field" smelter is not excessive. However, this analysis is based on the assumption that there is a nearby market for sulphuric acid. As described in section 7, the cost of acid neutralization must be added where it is more economically feasible than marketing sulphuric acid.

TABLE 20 ANALYSIS OF INVESTMENT COST AND UNIT PRODUCTION COST FOR COPPER SMELTER-REFINERY COMPLEX (41)

Section	Percentage of total investment cost	Percentage of total production cost
Concentrate handling	4.8	3.5
Matte smelting	15.3	16.7
Slag cleaning	3.9	6.2
Matte conversion	11.1	12.1
Acid plant	6.5	7.0
Anode casting	2.1	3.2
Copper refinery	13.5	12.4
Precious metals refinery	1.3	2.0
Effluent treatment	1.1	2.1
Site utilities	11.0	8.3
Site services	2.6	2.3
Oxygen plant	2.7	3.9
Working capital	7.7	-
Pre-operating expenses	3.4	-
Financing costs	13.0	-
Administration, selling, etc.	-	20.3
Total	100.0	100.0

In the case of new smelters, the requirement for sulphur containment alters the criteria for optimum economic location (45). Concentrates can be, and are, transported great distances, even in cases where sulphur containment is not a factor. Unlike sulphuric acid or liquid SO_2, concentrates do not require special railway tank cars or ships which must return empty from each trip. Furthermore, the tonnage of concentrate to be shipped is usually no greater, and sometimes considerably less, than the tonnage of metal plus the acid produced from the concentrate. It is, therefore, logical to locate new smelters in acid consuming areas, whenever possible.

Limitations of Existing Canadian Plants with Respect to Air Pollution Control

Existing older plants were not designed with control of SO_2 emissions in mind. Older smelters have multi-hearth roasters and fuel-fired reverberatory furnaces which produce large volumes of gases with low SO_2 content making sulphuric acid recovery or scrubbing impractical. The same problem exists in plants which have converters with gas-collecting hoods that are cooled by in-leakage of air. Added to this, converting in older plants is a batch operation, making sulphuric acid recovery from the resulting intermittently flowing gases difficult. Therefore, large capital expenditures are required to achieve a significant degree of sulphur containment from older smelters, not only for the sulphur fixation plants (usually sulphuric acid plants) but also for extensive remodelling of the smelters themselves. Such expenditures must be amortized over a period of 10 to 20 years and therefore require corresponding ore reserves to ensure economic operation of the smelter for this period. The remaining life of an orebody can therefore limit the availability of capital required for sulphur containment facilities.

For many existing plants it is not economical to market sulphuric acid because of remote location or market saturation. The cost of acid neutralization and gypsum impounding must be added. Table 22 shows the cost of neutralizing acid with limestone at the smelter site. This translates into an additional cost of 11 to 22 ¢ per kilogram of copper, depending on the sulphur/copper ratio in the concentrate (45).

TABLE 21 COST OF NEUTRALIZING SULPHURIC ACID WITH LIMESTONE AT THE SMELTER SITE (45)

Basis for Estimates		
Acid plant production to be neutralized		
t/yr 100% H_2SO_4	190 000	380 000
t/day 100% H_2SO_4	540	1 100
CAPITAL COST ($, June 1979 cost level)		
Neutralization plant[1]	5 818 000	9 272 000
Contingency @ 25%	1 454 000	2 318 000
	7 272 000	11 590 000
Auxiliary equipment and services including gypsum impounding	1 257 000	2 000 000
Total Capital Cost	8 529 000	13 590 000
PRODUCTION COST ($/t H_2SO_4 neutralized)		
Operating Cost		
Supervision	normally part of acid plant supervision	
Operating supplies	0.77	0.39
Utilities[2]	0.67	0.67
Operating supplies (incl. limestone)[3]	19.06	19.03
Maintenance[4]	0.99	0.79
Indirect costs[5]	0.64	0.32
Subtotal	22.13	21.20
Contingency @ 10%	2.21	2.12
Total operating cost	24.34	23.32
Capital Charges		
Amortization & interest @ 15 years and 10%/yr	5.89	4.68
Total Production Cost	30.23	28.00

[1] Includes engineering and construction overhead costs.

[2] Includes natural gas, water and electric power.

[3] Includes limestone (49% CaO) for acid neutralization and other operating supplies.

[4] @ 2.2%/yr of the total capital cost.

[5] Includes property taxes, insurance, legal and technical counsel, etc.

[6] June 1979 costs.

REFERENCES

1. "Guidelines for the Control of Emissions from the Non-Ferrous Metallurgical Industries". Prepared by the United Nations Economic Commission for Europe Task Force for the Development of Guidelines for the Control of Emissions from the Non-Ferrous Metallurgical Industries, Dec. 1979. (Draft)

2. "Auswurfbegrenzung Schwefeldioxid und Schwefeltrioxid aus Schwefelsaureanlagen", Verein Deutscher Ingenieure (edit.) VDI-Richtlinie 2298, Aug. 1970.

3. Biswas, A.K. and Davenport, W.G., "Extractive Metallurgy of Copper", International Series on Materials Science and Technology, Vol. 32, 2nd Edition, Edit.: Hopkins, D.W., Pergamon Press, 1980.

4. "Compilation of Air Pollutant Emission Factors", U.S. Environmental Protection Agency, Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, 2nd Edition, March 1975.

5. "Control of Sulfur Oxide Emissions in Copper, Lead, and Zinc Smelting", U.S. Bureau of Mines Information Circular No. 8527, 1971.

6. De Cuyper, Jaques, "Flotation of Copper Oxide Ores", Erzmetall, Vol. 30, Issue 3, pp. 88 - 94, March 1977.

7. Jansen, M.L. and Milligan, D.A., "Developments in Sulphur Disposal Techniques in Hydrometallurgy", Jour. of Metals, Vol. 27, pp. 13 to 17, 23, Jan. 1975.

8. "Japanese Copper Smelter for Total SO_2 Emission Control", Engin. and Mining Jour. pp. 13 to 17, 23, New York, 1972.

9. Jones, H.R., "Pollution Control in the Nonferrous Metals Industry 1972", Noyes Data Corp., New Jersey, U.S.A.

10. Kellog, H.H. and Henderson, J.M., "Sulfide Smelting of Copper", Paper for AIME, Las Vegas, 1976.

11. Mealey, Mike, "Japan's Tamano Copper Smelter: The Most Modern in the World", Engin. and Mining Jour., No. 6, pp. 130 - 131, 1972.

12. Melcher, Gerhard, Muller, Erich, Weigel, Horst, "Entwicklung, Grundlagen und Anwendung des KIVKET-Zyklonschmelzverfahrens mit reinem Sauerstoff fur verunreinigte Kupfererze", Erzmetall, Vol. 28, Issue 7/8, pp. 313-322, July/Aug. 1975.

13. Melcher, Gerhard, Muller, Erich and Weigel, Horst, "The KIVCET Cyclone Smelting Process for Impure Copper Concentrates", The Metallurgical Society of AIME, Jour. of Met., pp. 4 - 8, New York, N.Y., July 1976.

14. Melle, J. Van, "The Metallurgy of Copper", Het Ingieursbald, 46 (2), pp. 33 - 41, Feb. 1977.

15. Mills, L.A., Hallett, G.D. and Newmann, C.J., "Design and Operation of the Noranda Process Continuous Smelter", Extractive Metallurgy of Copper, Volume 1 - Pyrometallurgy and Electrolytic Refining, Edit.: Yannopoulos, J.C. and Agarwal, J.C., pp. 458 - 487, 1976.

16. Nagano, T. and Suzuki, T., "Commercial Operation of Mitsubishi Continuous Copper Smelting and Converting Process", Extractive Metallurgy of Copper, Volume I: Pyrometallurgy and Electrolytic Refining, Edit: Yannopoulos, J.C. and Agarwal, J.C., pp. 439 - 457, 1976.

17. Norman, T.E., "Nonpollution Autogenous Desulphuring Process Recovers Metals, Elemental Sulphur", 176, No. 8, pp. 92 - 97, 1975.

18. Paulson, D.L., et al., "Production of Blister Copper by Electric Furnace Smelting of Dead-Burned Copper Sulfide Concentrates", Bureau of Mines, Report of Investigation, No. 8131, Albany, Oregon, 1967.

19. Price, Frederick C., "Copper Technology on the Move", Engin. and Mining Jour., No. 4, pp. RR-WW, 1973.

20. "Progress in Smelter Emission Control", Environ. Sci. and Technol., Vol. 10, pp. 740 - 741, Aug. 1976.

21. Rampacek, C. and Dunham, J., "Copper Ore Processing - U.S. Practices and Trends", Mining Cong. Jour., Vol. 29, p. 20, Feb. 1977.

22. Roscrow, W.J., "Furnaces and Processes for Non-Ferrous Metal Recovery", Metallurgia and Metal Forming, pp. 272 - 274, 276, Aug. 1975.

23. Rosenbaum, J.B., "Sulfur Dioxide Emission Control in Japanese Copper Smelters", Bureau of Mines Information Circular No. 8701, 1976.

24. Schwartz, W. and Eisert, W., "Beispiele und Grenzen der Reinhaltung von Luft in Kupferhutten", Erzmetall, Vol. 25, Issue 10, pp. 505 - 511, Oct. 1972.

25. "Searching for Solutions to Pollution Problems", Engin. and Mining Jour., No. 6, pp. 178 - 183, 1972.

26. Semrau, Konrad T., "Control of Sulfur Oxide Emissions from Primary Copper, Lead, and Zinc Smelters - A Critical review", Jour. of Air Poll. Cont. Assoc., Vol. 21, No. 4, pp. 185 - 194, April 1971.

27. "The Effects of Pollution Control on the Nonferrous Metals Industries - Copper, Part II, Structure of Industry", Charles River Association, Inc., U.S. National Technical Information Service, Government Reports Announcements, 72(8): 41, April 1972.

28. Treilhard, Ronald G., "Copper State of Art", Engin. and Mining Jour., Issue 4, p. P - 2, 1973.

29. "Two Direct Smelting Processes Designed for Pollution Control in Copper Plants", Engin. Mining Jour., No. 4, p. 129, 1971.

30. "Ullmanns Encyklopadie der technischen Chemie", Vol. 11, 3rd Edition, Edit.: Wilhelm Forst, Munich, Berlin 1960.

31. Weigel, H. and Melcher, G., "Gehoren SO_2-Emissionsprobleme beim Kupferflammofenbetrieb der Vergangenheit an?", Metall., Vol. 29, Issue 5, pp. 458-465, May 1975.

32. Yazawa, A., "Trends in Modern Copper Smelting Processes", Erzmetall, Vol. 30, Issue 11, pp. 511-517, Nov. 1977.

33. Bailey, J.B.W. and Storey, A.G., "The Noranda Process after Six Years' Operation", Paper Presented at the 18th Annual Conference of Metallurgists, Sudbury, Ont., Aug. 1979.

34. Diaz, C.M., Sarren, H.C. and Solar, M.Y., "Inco's Oxygen Flash Smelting Process for Copper and Nickel Concentrates", Inco Metals Co., First Canadian Place, Toronto, Ont., M5X 1C4.

35. Boldt, J.R. and Queneau, P., "The Winning of Nickel", Longmans Canada Ltd., Toronto, Ont., 1967.

36. Neal, R.J. and Reyburn, R.A., "Converter Operating Practice at the Copper Cliff Smelter of the Inco Metals Company", Inco Metals Company, presented at 108th AIME Annual Meeting, New Orleans, Louisiana, Feb. 1979.

37. Antonioni, T.N., Church, A.D. and Partelpbeg, E., "Operation of the INCO Flash Smelting Furnace with Recycle of Converter Slags", Paper presented at the 18th Annual Conference of Metallurgists, Sudbury, Ont., Aug. 1978.

38. Thoburn, W.J. and Tyules, Pavla M., Optimization of TBRC Operation and Control at INCO's Copper Cliff Nickel Refinery.

39. "Afton Copper Smelter Process Economic at 27 000 Tons Yearly", Canadian Chemical Processing, Anon., March, 1979.

40. Daniels, R.A. and Jacquay, L.H., "TBRC - A New Smelting Technique", Paper No. A72-101, The Metallurgical Society of AIME.

41. Gray P.M.J. and Davy Powergas Ltd., "A Cost Basis For Development of Primary Copper Production Processes", Presented at an international symposium organized by the Institute of Mining and Metall., London, April 18-20, 1977.

42. Davenport, W.G., "Copper Smelting to the 2000", Paper presented at a Seminar "Extractive Metallurgy of Copper", McGill University, Nov. 12-16, 1979.

43. Non-ferrous Metal data 1979: American Bureau of Metal Statistics Inc., 420 Lexington Ave., New York, N. Y. 10017.

44. Argenbright, L.P. and Bennet Preble, "SO_2 from Smelters: Three Processes from an Overview of Recovery Costs", Environmental Science and Technology, Vol. 4, No. 7, pp. 554-561, July 1970.

45. "A Study of Sulphur Containment Technology in the Non-ferrous Metallurgical Industry", Environment Canada, Air Pollution Control Directorate, Report EPS-3-AP-79-8, April 1980.

46. Reimers J.H., Snelgrove S.R. and Taylor J.C. "Study of Emission Control Technology for Arsenic in the Non-ferrous Metallurgical Industry". Mining, Mineral and Metallurgical Division, Air Pollution Control Directorate, Environment Canada, Unpublished report, Jan. 1977.

47. Kellogg, H.H. and Henderson, J.M., "Energy Use in Sulphide Smelting of Copper", Extractive Metallurgy of Copper, Vol. I, editors, Yannopoulos, J.C. and Agarwal, J.C. AIME, New York, pp. 373-415, 1976.

48. Schultz, D.A., "Pollution Control and Energy Consumption at U.S. Copper Smelters", Jour. of Met. 30(1), pp. 14-20, 1978.

49. Mackiw, V.N. and Veltman, H., "Recovery of Metals by Pressure Hydrometallurgy - The Sherritt Technology", Paper presented in the People's Republic of China at a Seminar held during the 1979 Non-Ferrous Metals Mission.

50. Jusela, Jyrki and Makinen, Juho, "Advanced Smelting of Copper Concentrate by the Outokumpu Flash Smelting Method", The Second International Symposium on Management of Copper Resources, Lublin, Poland, April 27-28, 1977.

51. Harkki, S., Aaltonen, O. and Tuominen, T., "High Grade Matte Production with Oxygen Enrichment by the Outokumpu Flash Smelting Method", International Symposium on Copper Extraction and Refining, AIME 105th Meeting, Las Vegas, Nevada, Feb. 22-26, 1976.

52. Koch, W.E. and Pietsch, B., "Treatment of Oxide Copper Ores by Reduction and Ammoniacal Leaching", Translation of the Institution of Mining and Metallurgy, Vol. 83, pp. C14 - C17, London, 1974.

53. Shelly, T.R., "Sulphuric Acid and Ammoniacal Leaching of Sar Cheshmeh Oxide Copper Ore", Translation of the Institution of Mining and Metallurgy, Vol. 84, p. C174-C176, London, 1975.

54. Richards, K.J., "Annual Review of Extractive and Process Metallurgy Copper", Jour. of Met., Vol. 29, p. 20, March 1977.

55. Shirts, M.B., Bloom, P.A. and Mckinney, W.A., "Double Roast-Leach-Electrowinning Process for Chalcopyrite Concentrates", Bureau of Mines, Report of Investigation No. 7996, Salt Lake City, Dec. 1974.

56. Lutjen, George, "The Environmental Conformation in Copper", Engin. and Mining Jour., No. 4, p. E-I, 1973.

57. Herbert, I.C., "New Copper Extraction Processes", Jour. of Met., Vol. 26, pp. 16, 24, Aug. 1974.

58. Griffith, W.A., et al., "Development of the Roast-Leach-Electrowinning Process of Lakeshore", Jour. of Met., pp. 17-25, Feb. 1975.

59. Rosenzweig, Mark D., "Copper Makers Look to Sulfide Hydrometallurgy", Chem. Engin., pp. 79 - 81, Jan. 1976.

60. Biangardi, Sebastian and Pietsch, Harrnut, "Verarbeitung sulfidischer Kupfererze nach dem Lurgi-Metterberg (LM) - Verfahren", Erzmetall, Vol. 29, Issue 2, pp. 73 - 76, Feb. 1976.

61. Meixner, Michael J., "Der San-Telmo-Prozeb - ein hydrometallurgisches Verfahren zur Gewinnung von Kupfer und Zink aud komplexen Sulfiderzen". Erzmetall, Vol. 30, Issue 5, pp. 204 - 208, May 1977.

62. "Chemical Route to Copper" Chem. Engin., 77(8), New York, April 20 1970.

63. "Liquid Sulphur Dioxide", Anon., Chem. Engin., p. 320, Oct. 1955.

64. Henderson, J.M. and Pfeiffer, J.B., "How Asarco Liquifies SO_2 Off-Gas at Tacoma Smelter", Soc. of Mining Engin., p. 36, Nov. 1974.

65. "New Smelter, Acid Plant at Falconbridge to Improve Working Conditions and Efficiency", Anon., Can. Mining Jour., May 1978.

66. "Control of Copper Smelter Fugitive Emissions", U.S. Environmental Protection Agency, EPA-600/2-80-079, May 1980.

67. Gluschke, Wolfgang, Shaw, Joseph and Bension, Varon, "Copper: The Next Fifteen Years", D. Reidel Publishing Company, 1979.

68. World Metal Statistics, November 1980, Published by World Bureau of Metal Statistics.

69. Reimers, J.H., Snelgrove, S.R. and Taylor, J.C., "A Review of Process Technology for Mercury Control in Gases in the Non-Ferrous Metallurgical Industry", Unpublished Report prepared for the Mining, Mineral and Metallurgical Division of the Air Pollution Control Directorate of Environment Canada.

70. Antonioni, T.N., et al., "Inco Oxygen Flash Smelting of Copper Concentrate".

71. Weisenberg, I.J. et al., Pacific Environmental Services, Inc., "Feasibility of Primary Copper Smelter Weak Sulphur Dioxide Stream Control", EPA Contract No. 68-03-2398, July 1980.

72. Young, C.A. and Peters, T.H., "The Use of Vegetation to Stabilize Mine Tailings at Copper Cliff", Proceedings of the 15th Ontario Industrial Waste Conference, p. 68-77, June 1968.

73. Michelutti, R., "How to Establish Vegetation on High Iron-sulphur Mine Tailings", Can. Mining Jour., p. 54-58, Oct. 1974.

74. Spires, A.C., "Studies on the Use of Overburden Soils in Facilitating Vegetative Growth on High Sulphide Tailings", M.Sc. Thesis Laurentian University, 1975.