

Zero-Carbon/NORM-Free ZEGOR® 1 Carbochlorination of Copper ore

In addition to improving aluminum recovery, the multimetal ZEGOR® carbochlorination/MFBR² method is also applicable to reduction of copper-bearing ores. In such ores, it concurrently recovers all economic metals and coproduct radionuclides, in a first pass. The ZEGOR® method is more economic than the traditional process in that, in addition to obviating costly molten processes in ore reduction and alloying, the total cost of mining and mineral processing is distributed over the full family of economic metals and radionuclides, thus reducing the cost burden on the copper constituent, rendering safe NORM³-free ZEGOR® copper more competitive and profitable. ZEGOR® requires only two principal reactions in copper recovery whereas the traditional method calls for six process steps. As a remedy to cleansing co-located radionuclides that occur naturally in all copper deposits and other metallic ore bodies, multimetal ZEGOR® carbochlorination/MFBR can separate out the full series of radioactive isotopes, thus greatly reducing the known hazards in refining of such metallic ores. For example, ZEGOR® separates out elemental uranium from its oxides by converting to gaseous uranium chloride and then isolating the uranium chloride from, say, cupric or rare-earth chlorides. The distilled stable metal chlorides can be iteratively cleansed of any residual radioactive trace materials followed by reduction to elemental powdered form (depending on the end product application, to nanoscale size ranging up to dendritically-shaped interlockable particles for alloying and wrought processing).

Using a (CO,Cl)-carbochlorination system, the three-step process pathway for U_3O_8 reduction is: step-1, $U_3O_8 + 8*CO + 8*Cl_2 \rightarrow U_2Cl_{10} + UCl_6 + 8*CO_2$; step-2a, $U_2CL_{10} + 5*H_2 \rightarrow 2*U + 10*HCl$ and step-2b, $UCl_6 + 3*H_2 \rightarrow U + 6*HCl$. Step-2 has a combined product of 3U. Thereafter, the uranium is packaged for sale (to certified buyers only) and the HCl is converted back to chlorine and water as recycled inputs to the overall process, in accordance with: $2*HCl + 0.5*O_2 \rightarrow Cl_2 + H_2O$. Needless-to-say, a like procedure also applies to thorium oxide reduction.

Traditional refining begins with the crushing/grinding of the ore, e.g., chalcopyrite ore, then concentration by froth-flotation that yields an intermediate with 15-20% copper content. It should be understood that this percentage would be greater for bomite and chalcocite ores, which, although not discussed here, are deemed within the scope of this procedure. The main impurity in the concentrate is iron. However, nickel, gold, and silver are often present, along with traces of zinc, molybdenum, selenium, tellurium, cobalt, tin, and lead. Silica (sand) is added to the concentrate in a reverberator furnace and the mixture is heated to 1400-1450° C., to make a melt. Roasting with air converts much of the iron in the concentrate to an oxide (reactions 1 and 2) that reacts with the silica to form an iron silicate slag (reaction 3). The slag separates into an upper layer that is periodically removed, leaving a lower matte layer which is largely Cu₂S and FeS. The liquid matte is placed in a converter with more silica, and air is forced through it. In a similar fashion this transforms the remaining FeS first to FeO (reaction 2) and then to slag (reaction 3). The Cu₂S is partially converted to Cu₂O (reaction 4), which could react with any remaining FeS (reaction 5), and is finally converted to metallic or 'blister' copper (reactions 6 or 7). The blister copper, named for the appearance given by the bubbling of the SO₂ through the melt, is approximately 98-99% pure and can be further purified by fire refining (similar to the process above) and/or

¹ ZEGOR[®]: Zero-emission gasification/power and metallurgical ore reduction – the energy/metallurgy synergy

² MFBR: continuous manifold fluidized bed reactor

³ NORM: naturally occurring (primordial) radioactive materials with gamma-emitting decay progeny in mineral deposits

electrolysis. The electrolytic process uses the impure copper as anodes with purified copper cathodes in a solution containing H₂SO₄ and CuSO₄ as electrolytes. The electrolysis deposits quite pure (99 .95%) copper on the cathodes. However, further purification can be accomplished by zone refining (to 99.9999% purity). It should be noted that byproducts of copper refining, including silver, molybdenum, selenium, tellurium, gold, and sulfuric acid, may be produced in commercially significant quantities under the traditional process.

The traditional process reactions for chalcopyrite concentrate are six in number given that either reaction 6 or 7 is used as the final step, but not both:

```
reaction 1: 2*CuFeS_2 + 4*O_2 \rightarrow Cu_2S + 2*FeO + 3*SO_2
reaction 2: 2*FeS + 3*O_2 \rightarrow 2*FeO + 2*SO_2
reaction 3: 2*FeO + SiO_2 \rightarrow Fe_2SiO_4
reaction 4: 2*Cu_2S + 3*O_2 \rightarrow 2*Cu_2O + 2*SO_2
reaction 5: Cu_2O + FeS \rightarrow Cu_2S + FeO, followed by either
reaction 6 or 7:
reaction 6: Cu_2S + O_2 \rightarrow 2*Cu + SO_2 or
reaction 7: 2*Cu_2O + Cu_2S \rightarrow 6*Cu + SO_2
```

Under ZEGOR® a different process is employed. Ore crushing/grinding and froth-flotation, as discussed above, frontend the ZEGOR® Process for (CO,CI)-carbochlorination of copper-bearing ore; thereafter, however, multimetal ZEGOR® has only two principal reactions rather than the required six for the prior known treatment of the copper constituent. ZEGOR®'s carbochlorination/continuous manifold fluidized bed reactor (MFBR) (z-reaction 1) converts metallic compounds to metal chlorides, then separates/purifies the intermediates for input to a line of plasma gas reduction (zreaction 2) reactors for the production of copper powder that, in turn, allows for superior alloy formation (mechanically blended with other ZEGOR[®] metallic powders) and other higher performance in end products.

```
z-reaction 1: 5*CuFeS_2+7.5*Cl_2+4*CO \rightarrow 5*CuCl+5*FeCl_2+4*CS_2+2*SO_2 and
```

z-reaction 2/Plasma Gas Reduction: CuCl+0.5*H₂→Cu+ HCl,

with the following ZEGOR® secondary byproduct reactions for iron (contrary to the traditional method of treating the iron as an impurity in slag) and carbon disulfide conversion:

z-reaction 3/Plasma Gas Reduction: FeCl₂+H₂->Fe+ 2*HCl, with a portion of iron being pelletized for input to traditional steel making and the remainder left in various powdered forms for mechanical blending in a variety of alloys.

```
z-reaction 4: CS_2+3*O_2 \rightarrow CO_2+2*SO_2
```

Advantageously, expanding the ZEGOR® metallurgical module to include copper supports the coal-copper paradigm in regions that have contiguous coal and copper reserves. For example, the State of Montana, at 120 billion tons of coallignite, reportedly has the largest recoverable coal-lignite reserves of any state in the United States along with significant copper ore reserves. The clean-coal power generation of the ZEGOR® Process can be successfully applied to Montana coal, while serving as a strategic means to fulfill long-term US energy independence with zero-emission power generation. In synergistic fashion, it also applies to Montana copper. In this regard, globally, the most important and

voluminous copper ore is chalcopyrite (CuFeS₂); and it has two major derivatives that occur in Montana, in economic quantities, these are: bomite (Cu₅FeS₄-63% copper by weight) & chalcocite (Cu₂S-80% copper by weight). Chalcopyrite is also present in Montana, but reportedly, not at levels in the earth that allow for economic recovery. For the copper ores of Montana, the application of carbochlorination, like the application of (CO,CI)-carbochlorination to bauxite, provides the dual benefit of zero-emission power generation and NORM-free copper in powdered metallic form for ease of mechanical blending with other elemental powders for superior alloying. These considerations also apply to the strategic copper-bearing resources in the DRC-Zambia copper-belt.

Below, the ZEGOR® reactions for chalcopyrite, chalcocite and bomite concentrates (pelletized) are given: (native gold and silver traces are assumed to be present for process modeling purposes).

Chalcopyrite Concentrate Reaction1: 5*CuFeS + 7.5 *Cl₂ + 4*CO → 5*CuCl + 5*FeCl₂ + 4*CS₂ + 2*SO₂

Chalcocite Concentrate Reaction1: 5*Cu₂S + 5*Cl₂ + 2*CO → 10*CuCl + 2*CS₂ + SO₂

Bomite Concentrate Reaction1: $5*Cu_5FeS_4 + 17.5*Cl_2 + 8*CO \rightarrow 25*CuCl + 5*FeCl_2 + 8*CS_2 + 4*SO_2$

Gold (native) Reaction1: Au + 1.5*Cl₂ \rightarrow AuCl₃ (s) [auric chloride, a solid]

Silver (native) Reaction 1: Ag + $0.5*Cl_2 \rightarrow AgCl$ (s) [silver chloride, a solid]

Chalcopyrite, Chalcocite & Bomite Reaction2: $CS_2 + 3*O_2 \rightarrow CO_2 + 2*SO_2$, yielding various product compound multiples.

Chalcopyrite, Chalcocite & Bomite Reaction3/Plasma Gas Reduction: CuCl + $0.5*H_2 \rightarrow Cu + HCl$, yielding five, ten and twenty-five multiples of copper, respectively.

Chalcopyrite and Bomite Reaction4/Plasma Gas Reduction: FeCl₂ + H₂ \rightarrow Fe + 2*HCl, with both yielding five multiples Fe.

Gold Reaction2/Plasma Gas Reduction: AuCl₃ + 1.5*H₂ → Au + 3*HCl [assumes reactant auric chloride (on the left) is gaseous at higher process heat of the PGR reactor]

Silver Reaction2/Plasma Gas Reduction: AgCl + 0.5*H₂→ Ag + HCl [assumes reactant silver chloride (on the left) is gaseous at higher process heat of the PGR reactor]

The reactions are stoichiometric, and the relationship of the copper compounds on either side involves only Cu-I -- in accordance with "... all the known copper sulfides should be considered as purely monovalent copper compounds ..." in the URL: http://en.wikipedia.org/ wiki/ Copper (II) sulfide. Additionally, there are three oxidation levels for copper, Cu-I, Cu-II and rarely Cu-III.

The significance of Chalcopyrite, Chalcocite & Bomite Reaction 2 is to show reduction of CS₂ to compounds already routinely and economically managed in the overall ZEGOR® system. CO₂ is processed in the carbon recovery subsystem. and SO₂ is an input to the sulfuric acid production line, as described above. Thus, combining coal and copper carbochlorination provides greater efficiencies for the carbon recovery and sulfuric acid subsystems.