NOTATION

D = pipe diameter
N_c = critical Reynolds number predicted by Derman analysis
N^* = Reynolds number at the onset of early turbulence
p = hydrostatic pressure
Q^* = flow rate at the onset of early turbulence
S^* = wall shear rate at the onset of early turbulence
t = time
v_i = i^{th} component of the fluid velocity
x_i = i^{th} distance coordinate

Greek Letters

δ = solubility parameter
ρ = polymer solution density
μ = polymer solution viscosity
λ = polymer solution relaxation time associated with the Derman analysis
τ_{ij} = ij^{th} component of the shear stress tensor
τ_c = critical wall shear stress predicted by the Derman analysis
τ^* = wall shear stress at the onset of early turbulence

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Halogen Affinities—A New Ordering of Metals to Accomplish Difficult Separations

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Metallurgical separations utilize the relative ability of one metal to replace another in a compound. The desired metal is obtained in a pure form or more easily worked compound. In general, a "strong" metal replaces a "weak" metal in a solution of its salt, for example, iron added to a solution of copper sulfate replaces the weaker copper to yield metallic copper and iron sulfate.

Metals listed in order of their ability to replace one another in solutions form the electromotive series. The order of the metals in this series is not a function of temperature for aqueous solutions, and the displacement of a weaker metal in a salt by a free stronger metal may be complete and quantitative.

However, dry oxidation and reduction are equally important in extractive, physical, and mechanical metallurgy, and in the use of metals for coatings. Of growing importance is the reduction of oxides by hydrogen or by the displacement of the metal by a more active metal. For example, pure zinc may be produced by reducing zinc oxide by metallic iron.

A NEW ORDER OF METALS—CHLORIDE-FORMING AFFINITIES

A new ordering of metals according to their activity or strength depends on the affinity of a metal in an oxide to form its chloride. The resulting reaction allows one to separate readily metals from their ores or from each other. In a mixture of metallic oxides the metal of greatest affinity is the first to react with chlorine to form the chloride, provided the chlorine is present in only a limited amount. Alternatively a higher-affinity metal in its oxide form will displace chlorine from the lower-affinity metal chloride and, in so doing, will form the chloride of the stronger metal and the oxide of the weaker metal.

The reaction temperature is chosen to produce the chloride or oxychloride as a solid, liquid, or gas, as desired. While only a limited temperature range can be employed for reactions in aqueous solutions, one may use a much wider range with reactions of gases and solids.

The chloride-forming affinity of a metal at a given temperature is measured by the difference between the Gibbs free energy of its chloride (or in some cases its oxychloride) and its oxide. To order the metals (as well as sulphur, phosphorus, and silicon), relative chloride-forming affinities were determined experimentally and the free energies of the respective compounds calculated. The free energy differences determine the chloride-forming affinities, and hence determine the order of the metals. Table 1 shows the order for a few of the important metals and metalloids at 800° and 1300°C. Also shown are several shifts in the ordering at different temperatures. These shifts have been experimentally determined and confirmed by thermodynamic computations. They arise from changes in specific heats of the reactants and products. Advantage might be taken of this shift of ordering to separate metals by operating first at 1,300° and then at 800°C.

The usual electromotive displacement series, also shown in Table 1, illustrates a somewhat inverse relation to the new series based on the chloride-forming affinity.

If hydrogen is present in a fuel or otherwise in the reaction, it forms hydrochloric acid either with free chlorine or with chlorine present in a metallic chloride. In addition if the ore contains phosphorus or vanadium, the oxychlorides $POCl_3$ and VOCl may be formed, even though the chloride-forming affinities of phosphorus and vanadium are very low. Oxygen in the oxychlorides comes from oxygen, air, or one of the metallic oxides.

CHLORINATION OF METALS IN ORES

In proposing separations, the volatilities of the chlorides and of the oxychlorides must be known; Table 1 lists boiling temperatures of a few chlorides. Chlorination of a metal oxide often produces a volatile chloride and thus allows a separation from the reaction mass. This gaseous chloride may be contacted intimately and thoroughly with any other pulverant material. If this material is the oxide of another metal higher in the chloride-affinity series double decomposition takes place, which is characteristic of an oxidation-chlorination.

Oxidation-Chlorination. Chlorination displaces electrons from an element and is therefore an oxidative reaction. In chlorinating a metal oxide, for example, iron oxide by chlorine, the relative chemical instability of the volatile chloride formed compared to the oxide reverses the chlorination until an equilibrium is reached. Large amounts of energy are required for this reaction. Even at high temperatures, yields are small since the affinity of the resulting atomic oxygen for the iron is very much higher than the affinity of the elementary chlorine for the iron. However, the oxidation-chlorination of a two-metal interaction may differ markedly as shown below:

$$2Fe_2O_3(s) + 3TiCl_4(g) \leftrightarrows 4FeCl_3(g) + 3TiO_2(s)$$

Titanium is oxidized and iron is chlorinated; the reaction is rapid and complete; and since TiO_2 is nonvolatile, the separation is complete. $FeCl_3$ immediately vaporizes, so fresh ore surfaces can react. By contrast, in blast furnace reduction, metallic iron must first melt and run off or be diffused by a gaseous reductant to allow access to fresh ore surfaces.

Reduction-Chlorination. A reduction-chlorination is fueled by carbon. Its equivalent carbon monoxide would be a more effective reactant since solid carbon would have few points of contact with solid ore. Oxygen from the oxide forms the CO used in reduction-chlorination. An example might be:

$$Fe_2O_3(s) + 3CO(g) + 3Cl_2(g) \leftrightarrows 2FeCl_3(g) + 3CO_2(g)$$

This combined reduction and chlorination is exothermic and no external heat is required. Quantitative yields are readily obtained since the oxygen of the iron oxide is completely bound as CO_2; and the reaction products are gases.

Wescott attempted this reduction-chlorination of iron ores (*1*). Gaseous products were withdrawn, and ferric chloride was condensed as a solid. By using low temperatures, the formation of undesired chlorides with aluminum and silicon in the ore was minimized. Wescott operated at 400° to 450°C., but the reaction was too slow to be economic. With higher temperatures the reaction rate increased, but excessive chlorine was lost in forming large quantities of other chlorides. No production has resulted.

Reduction-chlorination produces titanium tetrachloride (*2*), but it has not been important in winning iron due to difficulties in separating the reaction products.

Dual Chlorination. Dual chlorination has been developed as a powerful separation technique. At temperatures chosen to volatilize the respective chlorides, the oxide ore is subjected first to an oxidation-chlorination, then to a reduction-chlorination. Chlorine gas and coke accomplish the reduction-chlorination to give a volatile metal chloride. This metal chloride is subjected to oxidation-chlorination,

TABLE 1. ORDER OF SOME COMMON ELEMENTS

Conventional electrochemical series (highest at bottom)	Chloride forming affinity from oxide (highest at top)		Boiling point of chlorides, °C.	
	at 1,300°C.	at 800°C.		
Cu	Cu	Pb	CuCl	1,690
Pb	Pb	Cu	$PbCl_2$	954
Sn	Zn	Zn	$ZnCl_2$	732
Ni	Co	Co	$CoCl_2$	1,050
Co	Ni	Sn	$SnCl_4$	114
Fe	Sn	Ni	$NiCl_2$	973
S	Fe	Fe	$FeCl_3$	319
V	Ti	Ti	$TiCl_4$	136
Ti	Ge	Ge	$GeCl_4$	84
Al	Al	Al	$AlCl_3$	183
	Si	Si	$SiCl_4$	58
	V	S	[*]SCl_2	59
	P	V	[*]VCl_4	164
	S	P	[*]PCl_3	76

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[*] Not formed here; instead, SO_2 (−10°C.), VOCl (127°C.), $POCl_3$ (105°C.).

where it interacts with the oxide of the metal highest in the chloride-affinity series to produce a volatile chloride. Any metal remaining in the ore after passing to the reduction-chlorination is immediately volatilized to a volatile chloride which is unaffected by the oxidation-chlorination.

SEPARATION OF METALLIC CHLORIDES

Successive Chlorination. Hypothetically, a number of metals, *A*, *B*, *C*, etc., occurring as oxides, may be separated from an ore which descends into a reactor composed of several stages. A reduction-chlorination in the bottom stage would drive off the volatile chloride of the metal *A* having the lowest affinity for chloride formation. This volatile chloride of *A* contacts the ore material in the next higher stage, interacts with the oxide of metal *B*, to be reoxidized to the oxide of *A* by forming the chloride of *B*. The *B* chloride is assumed to be volatile and flows to the next higher stage to interact with the oxide of *C* to give *B* oxide and *C* chloride, etc. Theoretically, a countercurrent reaction system operating with an ore having appropriate amounts of *A*, *B*, and *C*, could result in the following: an unreacted gangue in the lowest reactor, all of *A* as the oxide in the next reactor, all of *B* as the oxide in the next higher reactor, all of *C* as the volatile chloride leaving as a gas to be condensed.

Such a separation might be pictured as either a batch or a continuous operation, similar to a rectifying column in the usual distillation. Each chloride might then be separated almost quantitatively. Here the selective appearances of the metals as chlorides is due to the order of chloride-forming affinities, not to vapor pressures, as in a distillation.

While the order of the metals in increasing chloride affinities was chosen as *A*, *B*, *C*, there may be *any other order of volatilities or boiling points* of the respective chlorides. Actually, each stage must be operated at the temperature necessary to volatilize the metal chloride leaving that stage, and the temperatures of the several stages may be quite different than decreasing from bottom to top, as in a distillation.

Because no ore would have the exact molecular ratios of metals necessary to make these successive chlorinations quantitative, a dual chlorination with the exact amount of chlorine required must be used instead to remove the first chloride. Then a second dual chlorination, with its exact amount of chlorine, removes the second chloride, etc.

Fractional Condensation or Distillation of Volatile Chlorides. If, however, in an ore with several metals, the reduction-chlorination is carried far enough to chlorinate two or more of the metal oxides at the temperature necessary to volatilize the chloride with the highest boiling point, a mixture of the volatile chlorides of two or three metals distills. The vapor mixture may be separated by usual rectification. However, because the boiling points of the metal chlorides vary widely, fractional condensation of the vapors of different chlorides at the successively lower temperatures of their respective boiling points gives excellent separation.

Separation of Chlorides by Other Techniques. Metal chlorides may be removed from the top stage one-by-one at appropriate temperatures in the order of their chloride-forming affinities. If ore is fed to the top stage of a stagewise reacting system, the oxide of the metal with the highest chloride-affinity reacts with the volatile chlorides of other metals coming up to that stage, to give the volatile chloride and the nonvolatile oxides. These move with other solids to the next lower stage, countercurrently to the gas stream.

This oxidation-chlorination at the head of the system, that is, where the element of the greatest affinity is removed, acts like a heads-stripper in a distilling tower. All the volatile chlorides, except that of the metal highest in the affinity series, are held down and pass to the next lower stage as reflux. The volatile chlorides of the lower metals chlorinate the oxide of the highest-affinity metal in the ore feed and remove it as overhead product.

The oxidation-chlorination is less violent than the reduction-chlorination and acts as a more precise stripping or separating mechanism. Alternatively, if two, three, or all of the metals present in the system as impurities are high in the affinity series, they may pass off as a single overhead vapor stream to leave the desired metal to be removed as the solid oxide, or as the chloride, if it is nonvolatile. The mixed vapors of the chloride of metals high in the affinity series are fractionally distilled or separated otherwise.

Distillation never separates two components quantitatively. However, because of the preferential affinities of metals for chlorine, it is *theoretically* possible to achieve quantitative separations by this method. Because of the large masses of solids to be reacted countercurrently with a gas, it is *practically* impossible to achieve absolutely the same degree of contact throughout the whole body at the same instant. Hence, as in a distilling column, a greater number of stages in a reactor system may be used than would be necessary theoretically.

Chemical reactions are often conducted in a distillation column, where the products can be separated simultaneously. The proper stage at which to accomplish the chemical reaction is determined by the separations accomplished by rectification up to and above this stage. (For example, in the formation of a volatile ester and water from a volatile alcohol and a volatile aliphatic acid, the chemical reaction velocity and the relative velocities of the reactants and products control the design of the distillation system.) In these separations, there is also a comparable, though reverse, phenomenon which may be utilized in addition to the chemical reactions to produce the separations due to relative affinities. This phenomenon entails interrupting the sequence of the affinity-fractionating reactions to remove streams of two or more volatile materials, chlorides, or oxychlorides which have been formed. These volatile materials are then separated by fractional distillation, fractional condensation, or a physical or chemical reaction. Finally, the separated materials are removed to obtain the desired metal or re-introduced into the affinity-fractionating system.

Furthermore, differences in other physical properties have been utilized at some stage of the affinity-fractionation (usually at either end), as is often done with the overhead or bottom stream of a comparable distillation system. For example, nonvolatile chlorides of alkali or alkali-earth metals remain in the final gangue. They dissolve in water and may be separated by wet processing. In addition, chlorides and oxychlorides in the overhead vapor stream, along with a metal chloride, hydrogen chloride, and other gases are readily separated by chemical processing. Other physical or chemical reactions of particular metals may be utilized at some one of the intermediate stages to interrupt the basic separation by affinity-fractionation, just as chemical or physical operations may interrupt the separations by fractional distillation.

Bromine often may be used in place of chlorine; iodine is less useful and too expensive. Many bromides are less volatile, and bromine and hydrobromine acid may be easier to recover. Losses of either are low in the cyclic processes.

EXTRACTION AND SEPARATION OF IRON

The Halomet Process (3, 4) uses the above techniques to produce iron and any other valuable elements present from almost any iron ore. All products may be obtained in a pure form and in nearly quantitative amounts. Reduction-chlorination produces a gas mixture of the volatile chlorides of iron and other elements. When the gas mixture is passed to an oxidation-chlorination reactor with more iron ore at the same high temperature, it oxidizes the nonferrous chlorides, yielding iron chloride in the vapor, as well as sulfur, phosphorus, and vanadium as SO_2, $POCl_3$, and $VOCl$, respectively. These more volatile impurities appear as a gas for subsequent recovery as sulfuric acid, phosphoric acid and vanadium oxide, while the $FeCl_3$ condenses at a temperature below 300°C. $FeCl_3$ is converted with hydrogen to produce pure iron powder and HCl or burned with oxygen to yield chlorine for reuse and pigment grade Fe_2O_3 for reduction to pure iron.

If titanium is present, a separate dual chlorination of the first gangue gives $TiCl_4$ or TiO_2. If Zn, Cr, Co, or Ni are in the ore, they appear as nonvolatile chlorides in the gangue and may be readily leached out and separated by wet processing.

Operation of the Halomet process in a pilot plant of substantial size to produce pure iron from ores which otherwise are uneconomical to use has shown a lower production cost and has provided for recovery of impurities in a practically pure form for sale.

SEPARATION OF NONFERROUS METALS

The amount of chlorine supplied to the dual chlorination is the stoichiometric amount required by the metal of the highest chloride-affinity. The gaseous chloride is discharged from the oxidation-chlorination and condensed in a practically pure form. (Some additional chlorine may be required for other reactions.) If traces of chlorides of other metals are present in these vapors, they often may be eliminated by adsorption on activated carbon or silica-gel. Other metals leave the reactor in the solids or gangue passing out from the reduction-chlorination. These metals are usually oxides or nonvolatile chlorides if they are of high affinity. A second dual-chlorination system then uses the stoichiometric amount of chlorine for the metal with the next highest affinity at a temperature sufficiently high to volatilize its chloride. The process is repeated, utilizing additional processing by chemistry and extractive metallurgy as may be warranted. For example, if magnesium is present, its nonvolatile chloride $MgCl_2$ is leached from the residual gangue.

Rutile, the desired starting point for titanium metal and TiO_2 pigment, may sell for five times as much as ilmenite on a titanium basis. With a dual-chlorination and some simple additional steps, pure $TiCl_4$ or 99%-pure white synthetic rutile has been made from ilmenites containing many different impurities. This synthetic rutile is immediately suitable for some pigment uses.

Manganese. Nowak (5) determined the heats of the chlorination reactions, the approximate equilibrium constants, and the thermodynamic free energy balances. He also demonstrated the chlorination and other steps necessary to win Fe, Mn, and other products from manganiferous iron ores. This work corroborated earlier data (6). Manganese has a higher chloride-affinity than does iron. Consequently, any volatile chloride of iron or lower-affinity metals reacts with manganese oxide to yield manganese chloride and oxides of the lower-affinity metals, including iron. All products appear as nonvolatile solids. Fe_2O_3 is then converted to the volatile $FeCl_3$ by reduction-chlorination; and alumina and silica, if present, can be left unchanged by correct metering of the chlorine added.

Tin, Lead, Zinc. Two or more dual chlorinations in series may be used to separate these and other metals, such as iron and aluminum, from many ores or concentrates and from one another.

Alumina and Iron from Clays, Shales, and Red Muds. One or more dual chlorinations can separate iron and aluminum as the chlorides or oxides from clays or shales. Relatively expensive bauxite is used for all aluminum produced today. In the Bayer process a large fraction of bauxite ends up as "red mud," (which is insoluble in the caustic soda solution used) and accumulates to present a major disposal problem and cost. Typically, a dry weight analysis of the mud shows: Al_2O_3-26.0%, Fe_2O_3-50.5%, SiO_2-8.5%, TiO_2-6.0%, Na_2O-7.0%, CaO-2%. In such a material, consider two successive dual chlorinations. In the first chlorination, pure $FeCl_3$ is separated. The second chlorination separates $TiCl_4$ (with SO_2 and HCl) and CO + CO_2 from the coke, leaving $CaCl_2$, NaCl, Al_2O_3 and SiO_2 as the residual solids. The $CaCl_2$ and the NaCl are washed out for discard. The alumina-silica mixture is recycled to the Bayer process, or a third dual chlorination may be employed to produce $AlCl_3$ and a gangue of silica.

Al_2O_3, P_2O_5, and Fe from Slimes from Phosphate Rock Beneficiation. In Florida, 30 million tons of solids from phosphate rock beneficiation are disposed annually at a cost of $10 million. These "wastes," plus hundreds of millions of waste tons from previous operations, contain on a dry basis: 18 to 20% Al_2O_3, 7 to 8% Fe_2O_3, 30 to 32% SiO_2, 16 to 18% P_2O_5, 19 to 20% CaO, and minor amounts of the oxides of Ti, Mg, Mn, Na, and K. Again, a dual chlorination might be used to remove phosphorus as $POCl_3$ and then H_3PO_4, an important source of revenue. Iron would come out as $FeCl_3$. Aluminum may be taken out as $AlCl_3$ in a second dual chlorination, or it may be left as Al_2O_3 in the residue, which is principally SiO_2 and chlorides of the alkali and alkali earth metals.

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