A Comparison of Two Novel Non-Ferrous Metal Recovery Equations: Development, Similarity and Industrial Significance

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The recovery of non-ferrous metals in oxidative sulfide smelting and converting processes and within reductive oxide smelting processes has been previously analyzed using two similar equations which express recovery in terms of iron transfer and a distribution coefficient. A detailed comparison will show that the equations are mathematically identical but with one equation validated only for constant distribution coefficients. The wider applicability of the equation and implications for optimization of metal recovery are discussed.

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TWO metal recovery equations which conveniently express non-ferrous metal recovery in terms of iron transfer and a readily measured distribution coefficient will be compared. The equation was first used by Grimsey^[1–5], a similar equation was subsequently used by Jones *et al.*^[6–11] However, the initial equation has never been discussed by Jones *et al.* and has only been referenced once^[8] by these authors. The development of the two equations, their relationship, and their relevance will be considered here. They will be referred to, respectively, as the Grimsey and Jones equations in this discussion.

Sulfur and iron are the major impurities within sulfide mineral concentrates which contain valuable nickel, copper and cobalt. The impurities are removed by oxidation of matte (molten sulfide) with air, with sulfur reporting to gas as SO₂ and iron reporting to molten silicate slag as iron oxide. It is well understood that the recovery of non-ferrous metals to liquid sulfide matte decreases as more iron impurity is oxidized and transferred to slag since non-ferrous metal is transferred along with it. The important relationship between non-ferrous metal recovery and iron transfer can be described by a novel metal recovery equation using a distribution coefficient, as reported by Grimsey,^[1–5] namely:

$$R_{Me} = \frac{1 - y}{1 - y + \frac{y}{K'_{Me}}} \quad [1]$$

R_{Me} represents fractional metal recovery to matte, y represents the fraction of iron impurity reporting to

the slag and K'_{Me} represents a distribution coefficient defined as:

$$K'_{Me} = \frac{[Me \text{ pct}]}{(Me \text{ pct})} \frac{(Fe \text{ pct})}{[Fe \text{ pct}]} \quad [2]$$

where $[Me \text{ pct}]$ and $(Me \text{ pct})$ represent the respective percents of non-ferrous metal Me (e.g., Ni, Cu, Co) in matte and slag and $[Fe \text{ pct}]$ and $(Fe \text{ pct})$ represent the respective percents of iron. The fact that these four concentration terms could be grouped within a single distribution coefficient to succinctly describe metal recovery was not initially obvious. An iron mass balance, previously unpublished, led to this recognition.

Consider, for example, the distribution of iron and any other metal Me within a non-ferrous matte/slag sulfide smelting system. If fraction y of iron reports to slag, the mass of Me in slag per ton of iron is given by $\frac{(Me \text{ pct})}{(Fe \text{ pct})} y$ and the mass of Me in matte per ton of iron is given by $\frac{[Me \text{ pct}]}{[Fe \text{ pct}]} (1 - y)$. Total Me is $\frac{(Me \text{ pct})}{(Fe \text{ pct})} y + \frac{[Me \text{ pct}]}{[Fe \text{ pct}]} (1 - y)$ and the fractional recovery to matte (R_{Me}) can be expressed as

$$R_{Me} = \frac{\frac{[Me \text{ pct}]}{[Fe \text{ pct}]} (1 - y)}{\frac{[Me \text{ pct}]}{[Fe \text{ pct}]} (1 - y) + \frac{(Me \text{ pct})}{(Fe \text{ pct})} y} \quad [3]$$

Division throughout by $\frac{[Me \text{ pct}]}{[Fe \text{ pct}]}$, with rearrangement, gives Eq. [1]:

$$R_{Me} = \frac{(1 - y)}{(1 - y) + \frac{(Me \text{ pct})}{[Me \text{ pct}]} \frac{[Fe \text{ pct}]}{(Fe \text{ pct})} y} = \frac{1 - y}{1 - y + \frac{y}{K'_{Me}}} \quad [4]$$

Equation [1] is simply a unique expression of the mass balance and hence must be true over the full range of

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iron transfer (y) relevant to a separation process. The equation places no constraint on the value of the distribution coefficient K'_{Me} but will only be useful for process control and monitoring if K'_{Me} remains constant or changes in a predictable manner with change in y . During nickel sulfide converting, for example, K'_{Co} was found to have a constant value,^[1-5] K'_{Ni} to have a constant value after discounting entrainment,^[5] and K'_{Cu} to have a value which varied as a function of $\log[\text{Fe pct}]$.^[3,5]

During sulfide converting the transfer of iron to slag occurs in multiple stages rather than in a single stage as defined by Eq. [1]. However, the equation can be expanded for multiple stages. If slag is taken off in two stages, for example, in which iron fraction y_1 is removed in the first stage and iron fraction y_2 in the second stage, where y_1 and y_2 are fractions of the original iron in matte, then Eq. [1] expands to give:

$$R_{Me} = \frac{(1 - y_1)(1 - y_1 - y_2)}{\left(1 - y_1 + \frac{y_1}{K'_{Me}}\right)\left(1 - y_1 - y_2 + \frac{y_2}{K'_{Me}}\right)} \quad [5]$$

The general equation for n stages, originally verified by Dr Mark Lucas,^[12] takes the form:

$$R_{Me} = \prod_{i=1}^n \left(\frac{1 - \sum_{j=1}^i y_j}{1 - \sum_{j=1}^i y_j + \frac{y_i}{K'_{Me}}} \right) \quad [6]$$

Significantly, because the single stage Eq. [1] and multistage Eq. [6] are both an expression of a mass balance, they would be applicable to any two-phase separation process, whether metallurgical or otherwise, and could provide valuable relationships for process monitoring and control when the transfer of one species is linked to the transfer of another such that K'_{Me} has a reproducible value.

Jones and co-workers subsequently developed and utilized an equation to describe the recovery of non-ferrous metal (Co, Ni, Cr) and PGM's within liquid ferroalloys produced during the smelting of oxides with carbonaceous reductant^[6,8-11] and for converting of alloy with oxygen.^[7] The equation expressed the fractional recovery of non-ferrous metal (R_{Me}) in terms of the fractional recovery of iron (R_{Fe}) and a constant distribution coefficient (K_γ), according to:

$$R_{Me} = \frac{K_\gamma R_{Fe}}{1 - (1 - K_\gamma) R_{Fe}} \quad [7]$$

In contrast to the first approach, in which the recovery equation was identified directly from a mass balance, the Jones equation was developed,^[6,9] by initially using thermodynamics to identify a distribution coefficient that would remain constant throughout the separation process. Mole balances and recovery equations based on moles, were then substituted within the distribution coefficient and rearranged to derive Eq. [7].

The development was illustrated using the distribution of cobalt and iron within ferroalloy after carbonaceous reduction of oxides in the presence of slag. Under

this scenario, the final distribution was reasonably assumed to be controlled near equilibrium by a divalent metal/iron exchange reaction, according to:

for which:

$$K_8 = \frac{a_{Co}}{a_{CoO}} \frac{a_{FeO}}{a_{Fe}} = \left(\frac{\gamma_{Co} x_{Co}}{\gamma_{CoO} x_{CoO}} \right) \left(\frac{\gamma_{FeO} x_{FeO}}{\gamma_{Fe} x_{Fe}} \right) \\ = \left(\frac{\gamma_{Co}}{\gamma_{Fe}} \frac{\gamma_{FeO}}{\gamma_{CoO}} \right) \left(\frac{x_{Co}}{x_{CoO}} \frac{x_{FeO}}{x_{Fe}} \right) \quad [9]$$

where a is activity relative to liquid standard state, γ is activity coefficient and x is mole fraction. Given the chemical similarity of iron and cobalt, γ_{Co}/γ_{Fe} within the alloy and $\gamma_{FeO}/\gamma_{CoO}$ within the slag were considered likely to remain constant. An isothermally constant distribution coefficient K_γ could then be defined in terms of the activity coefficient ratio and equilibrium constant K_8 , through rearrangement of Eq. [9] according to:

$$\left(\frac{\gamma_{Fe}}{\gamma_{Co}} \frac{\gamma_{CoO}}{\gamma_{FeO}} \right) K_8 = \left(\frac{x_{Co}}{x_{CoO}} \frac{x_{FeO}}{x_{Fe}} \right) = \left(\frac{n_{Co}}{n_{CoO}} \frac{n_{FeO}}{n_{Fe}} \right) = K_\gamma \quad [10]$$

The initial moles of metals and oxides were then, respectively, defined as n_{Co}^o , n_{Fe}^o , n_{CoO}^o , n_{FeO}^o to give the following mass balance and recovery expressions:

$$n_{Co} = n_{Co}^o + n_{CoO}^o - n_{CoO} \quad [11]$$

$$n_{Fe} = n_{Fe}^o + n_{FeO}^o - n_{FeO} \quad [12]$$

$$n_{CoO} = (1 - R_{Co})(n_{Co}^o + n_{CoO}^o) \quad [13]$$

$$n_{FeO} = (1 - R_{Fe})(n_{Fe}^o + n_{FeO}^o) \quad [14]$$

Substitution for n_{Co} , n_{CoO} , n_{Fe} and n_{FeO} (Eqs. [11] to [14]) within the distribution coefficient expression (Eq. [10]), with rearrangement, then yielded the recovery equation (Eq. [7]).

Since y in the single stage Grimsey equation (Eq. [1]) represents the fraction of iron reporting to slag, the fractional recovery of iron to alloy in the Jones equation (R_{Fe}) can be replaced by $1 - y$. Substitution for R_{Fe} in the Jones equation (Eq. [7]) gives:

$$R_{Me} = \frac{K_\gamma R_{Fe}}{1 - (1 - K_\gamma) R_{Fe}} = \frac{K_\gamma (1 - y)}{1 - (1 - K_\gamma) (1 - y)} \\ = \frac{K_\gamma (1 - y)}{(1 - y) K_\gamma + y} = \frac{1 - y}{1 - y + \frac{y}{K_\gamma}} \quad [15]$$

Thus, the Jones equation takes the same form as the single stage Grimsey equation; further, the equations are mathematically identical since $K_\gamma = K'_{Me}$ according to:

$$K_\gamma = \frac{n_{Me}}{n_{MeO}} \frac{n_{FeO}}{n_{Fe}} = \frac{[n_{Me}]}{[n_{Me}]} \frac{(n_{Fe})}{[n_{Fe}]} = \frac{[Me\ pct]}{(Me\ pct)} \frac{(Fe\ pct)}{[Fe\ pct]} = K'_{Me} \quad [16]$$

The Jones equation can also be derived if $(1 - y)$ in the single stage Grimsey equation is replaced by R_{Fe} . As a result, the R_{Me} versus R_{Fe} figures presented by Jones *et al.*^[6–11] are mirror images of the R_{Me} versus y figures presented by Grimsey^[1–4] and the concepts discussed are similar.

Significantly, when Eqs. [10] to [14] are combined in the Jones derivation to yield Eq. [7], the result, in common with Eq. [1], is simply a unique expression of the mass balance. Thus, the underlying validity of Jones equation has no dependence on thermodynamics and it is coincidental that the divalent equilibrium constant chosen for the derivation gave the same distribution coefficient as that required by the mass balance.

Consider, for example, the outcome if a monovalent rather than a divalent *Me*/iron exchange equilibrium was chosen to define a constant distribution coefficient K_γ^* for the recovery equation. For a monovalent *Me*/iron exchange, the distribution coefficient based on the equilibrium constant would take the form:

$$\begin{aligned} K_\gamma^* &= \frac{x_{Me}^2}{x_{Me_2O}} \frac{x_{FeO}}{x_{Fe}} \cong 2x_{Me} \left(\frac{x_{Me}}{x_{MeO}} \frac{x_{FeO}}{x_{Fe}} \right) \\ &= 2x_{Me} \left(\frac{n_{Me}}{n_{MeO}} \frac{n_{FeO}}{n_{Fe}} \right) = 2x_{Me} K_\gamma \end{aligned} \quad [17]$$

Here K_γ is the distribution coefficient ultimately required in the recovery equation to meet the mass balance. Thus, when Eqs. [11] to [14] are substituted into Eq. [17] and rearranged, the derived equation would be identical to Eq. [7] except that K_γ would be replaced by $K_\gamma^*/2x_{Me}$. Clearly, if K_γ^* remains constant, the distribution coefficient K_γ mandated by the mass balance, will vary as the mole fraction of *Me* in the alloy changes during the process. A similar outcome will result if a trivalent metal exchange is used as a template to identify a constant distribution coefficient.

Thus, based on its derivation, the Jones equation strictly only applies to divalent metals which equilibrate with iron through a dominant exchange reaction. An additional limitation is that the metal must predominantly be dissolved rather than mechanically entrained within slag such that an equilibrium constant can determine the distribution. However, notwithstanding these constraints, Jones *et al.*^[9] have reasonably fitted the recoveries of Co, Ni, Cr and PGM's within oxide reduction systems using constant K_γ values.

Originally, Eq. [1] was developed and utilized within an industry and government co-sponsored project^[1] aimed at understanding the recovery of cobalt within the Kalgoorlie Nickel Smelter using both laboratory and plant data. A major outcome of the study was the recognition that cobalt recovery could be monitored, controlled and optimized through consideration of iron transfer as summarized within Eq. [1]. The concept was subsequently used for the simulation of Ni, Co and Cu

recoveries within an industrial Peirce Smith converter operation which involved significant iron transfer from matte to slag.^[5]

The industrial significance of Eq. [1], however, extends beyond its application to nickel smelting and converting, firstly because it can potentially be applied to a range of other separation processes as initially discussed, and secondly because it likely supports valuable industrial guidelines for the monitoring and optimization of metal recovery within other non-ferrous smelting processes. These are processes where iron is a major impurity and where the non-ferrous metal oxide is less stable than ferrous oxide, (*i.e.*, $K'_{Me} > 1$) such that Fe can be preferentially oxidized compared to *Me* to affect separation.

The application of Eq. [1] to nickel smelting and converting processes has highlighted the following guidelines for managing non-ferrous metal recovery:

- (1) The so-called L_{Me} ratio, where $L_{Me} = \frac{[Me\ pct]}{(Me\ pct)}$, has been commonly used as an indicator of metal recovery performance, but Eq. [1] shows that recovery depends on $\frac{[Me\ pct]}{(Me\ pct)} \frac{(Fe\ pct)}{[Fe\ pct]}$ as defined by K'_{Me} rather than L_{Me} alone.
- (2) It is generally considered that increase in slag mass through addition of fluxes for liquidus or viscosity control will decrease metal recovery; however, a mass increase alone will not change the ratio of dissolved metals $\frac{(Fe\ pct)}{(Me\ pct)}$ or K'_{Me} and affect metal recovery, except in the presence of significant acid-base interactions (discussed below).
- (3) Processes with larger K'_{Me} values at a given fractional iron transfer y , will give higher, but not proportionally higher recoveries of *Me*; *i.e.*, process recoveries cannot be directly compared using K'_{Me} values.
- (4) Eq. [1] quantifies the well-understood concept that recovery of *Me* with a defined end-point iron content (*i.e.*, with fixed [Fe pct]), will decrease with increase in *Fe/Me* in feed, or with any downstream addition of iron, since both will increase the iron transfer required to achieve the end point.
- (5) It follows from (4), that a fair comparison of non-ferrous metal recovery within two different processes or flowsheets can only be made at a point where the fractional iron transfer is the same for both.
- (6) It is well understood that as iron transfer approaches the end point, the recovery of non-ferrous metal decreases more rapidly. This is reflected within Eq. [1], since with $K'_{Me} > 1$, the recovery of *Me* falls at an increasing rate as the fractional iron transfer to slag increases. This can be shown from the derivative of Eq. [1], with the fall increasing very rapidly after y exceeds ~0.9. However, the recovery of *Me* can be increased if iron is transferred in a series of steps as achieved using Peirce Smith Converters. In this case, Eq. [6] can be used with Solver in Excel to vary the y 's to maximize R_{Me} , subject to process constraints. Further, if K'_{Me} is constant, as for Ni and Co in nickel converting,^[5] recovery can be optimized for both metals using the same series of steps.^[1]

Ultimately, the industrial value of K'_{Me} can only be obtained by fitting plant data, but the presence of a dominant divalent iron exchange equilibrium can influence the magnitude of K'_{Me} and also dictate how change in temperature and addition of flux to slag will affect K'_{Me} .

The distribution of cobalt within oxidative sulfide matte/slag smelting and converting, for example, is likely controlled by the equilibrium exchange of iron between matte and slag^[1–4] according to:

for which it is readily shown that:

$$K'_{Co} = \frac{[\text{Co pct}][\text{Fe pct}]}{(\text{Co pct})[\text{Fe pct}]} = \left(\frac{\gamma_{\text{CoO}} \gamma_{\text{FeS}}}{\gamma_{\text{FeO}} \gamma_{\text{CoS}}} \right) \frac{1}{K_{18}} \quad [19]$$

where γ is the activity coefficient relative to the pure liquid standard state and K_{18} is the equilibrium constant for reaction [18].

Since the exchange reaction [18] is endothermic, the equilibrium constant K_{18} increases with increase in temperature, such that K'_{Co} decreases (cf. Eq. [19]) which will also decrease the recovery of cobalt.

The effect of flux addition to slag on cobalt recovery will depend on how the addition affects the $\gamma_{\text{CoO}}/\gamma_{\text{FeO}}$ in slag (cf. Eq. [19]) and not on how it affects γ_{CoO} alone. Experimental data^[1] show that the value of γ_{CoO} is increased by addition of MgO, Al₂O₃ and CaO in slag and decreased by the addition of SiO₂ due to acid-base interactions. However, the $\gamma_{\text{CoO}}/\gamma_{\text{FeO}}$ ratio remains relatively constant with addition of MgO and Al₂O₃, decreases slightly with CaO addition, and increases with SiO₂ addition.^[1] On this basis, increases of MgO and Al₂O₃ in slag should not significantly affect cobalt recovery; however, increase in CaO should slightly decrease the recovery, and increase in SiO₂ should increase it.

In summary, a novel recovery equation developed to describe non-ferrous metal recovery from sulfide smelting and converting processes is shown to provide a valuable template for the assessment and monitoring of non-ferrous metal recovery as a function of iron transfer, through use of an easily measured distribution coefficient. Since the equation is derived from a mass balance without any thermodynamic restrictions, it would be applicable to any two-phase separation process in which the recovery of one species can be related to that of another. A similar equation, subsequently developed to describe non-ferrous metal recovery from reduction smelting, is shown to be mathematically identical to the single stage version of the original equation. However, it was derived using

thermodynamic considerations which appear to validate its use only for divalent metals which give constant distribution coefficients.

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