On geological interpretations of crystal size distributions: Constant vs. proportionate growth

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ABSTRACT

Geological interpretations of crystal size distributions (CSDs) depend on understanding the crystal growth laws that generated the distributions. Most descriptions of crystal growth, including a population-balance modeling equation that is widely used in petrology, assume that crystal growth rates at any particular time are identical for all crystals, and, therefore, independent of crystal size. This type of growth under constant conditions can be modeled by adding a constant length to the diameter of each crystal for each time step. This growth equation is unlikely to be correct for most mineral systems because it neither generates nor maintains the shapes of lognormal CSDs, which are among the most common types of CSDs observed in rocks. In an alternative approach, size-dependent (proportionate) growth is modeled approximately by multiplying the size of each crystal by a factor, an operation that maintains CSD shape and variance, and which is in accord with calcite growth experiments. The latter growth law can be obtained during supply controlled growth using a modified version of the Law of Proportionate Effect (LPE), an equation that simulates the reaction path followed by a CSD shape as mean size increases.

INTRODUCTION

There may be a serious flaw in application of the popular crystal size distribution (CSD) analysis method that uses population-balance modeling. This technique for analyzing CSDs was developed in the chemical engineering industry (Randolph and Larson 1971) and first applied to rocks by Marsh (1988). The problem discussed here differs from the one recently proposed by Pan (2001) concerning inherited correlation, the validity of which has been debated (Schaeben et al. 2002; Marsh and Higgins 2002; Pan 2002a, 2002b). The present problem is related to the assumption, made in most geological papers on the subject, that, once nucleated, all crystals will grow at the same linear rate, a rate that is independent from crystal size.

The solution to the population-balance equation used with these (and other) assumptions is:

\[ \ln(n) = \ln(n^0) - \frac{L}{G \tau} \]  

(1)

where \( n \) is the crystal population density (number of crystals per given size class per unit volume); \( L \) is the characteristic crystal size, measured for a consistent linear direction in the crystals; \( n^0 \) is the population density of nucleus-size crystals (it is \( n \) when \( L \) approaches zero); \( G \) is the mean linear growth rate, which is independent of \( L \); and \( \tau \) is the average crystal residence time in the system (Randolph and Larson 1988; Marsh 1988; Cashman and Marsh 1988; Mersmann 2001).

Equation 1, which is used both by chemical engineers and by geologists, is a greatly simplified version of the more general population-balance equation. According to Mersmann (2001), the derivation and application of Equation 1 assumes ideal mixing in a continuously operated industrial crystallizer that is running in a steady-state condition in which there are no fluctuations in operating conditions with respect to time. The feed solution is generally free of crystals, and the slurry is removed continuously at a single flow rate. There is assumed to be no crystal breakage, attrition or agglomeration, and solution and crystals have the same mean residence time (\( \tau \)) in the crystallizer. In addition, the linear crystal growth rate is assumed to be independent of crystal size, which is the assumption that is the focus of the present paper. Also according to Mersmann (2001, p. 156), Equation 1 applies only to MSMPR (mixed suspension, mixed product removal) crystallizers.

It will be shown that a linear growth rate is not independent of size, but, rather, that growth rates which generally increase with crystal diameter provide a more robust description of observed CSDs for most crystallizing systems. Other investigations using alternative calculation methods, which have assumed a growth rate that is independent of crystal size (e.g., Kretz 1966; Carlson et al. 1995), and constant growth equations that are discussed in Nielson (1964), Kirkpatrick (1981), Randolph and Larson (1988), and Lasaga (1998) also may be unrealistic. Therefore, geologic conclusions drawn from Equation 1 and from the alternative methods are questionable. These conclusions involve both qualitative models of geologic processes, such as the movement, mixing, and crystallization of magmas, and quantitative calculations such as nucleation rates, residence times, or growth rates for crystals in magmatic and metamorphic rocks.

A COMPARISON BETWEEN GROWTH EQUATIONS

Size-independent (constant) crystal growth, for a given crystal in a population of crystals, is described by: