



# A modified shrinking core model for the reaction between acid and hetero-granular rough mineral particles



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## ABSTRACT

The liquid–solid heterogeneous non-catalytic reaction between acid and minerals is the foremost principle of matrix acidizing. Previous mathematical models failed to describe the acid etching issue of rock particle clusters with the property of fractal surface in a three-dimensional space. We apply fractal geometry principles to characterize the area and volume of the rough rock particles on the basis of a mathematical model of a single particle. Based on chemical reaction kinetics and mass transfer theory, we present a modified shrinking core model for the acid–rock reaction of a mineral particle cluster that is undergoing a surface reaction. Using logarithmic normal distribution functions to describe the grain distribution of rocks, we describe the variations of the extent of leaching under surface reaction control. Our analysis indicates that clusters with larger fractal dimensions, smaller mean sizes and less disperse particles will be less dissolved when most of the other factors are kept constant.

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## 1. Introduction

Matrix acidizing has been commonly used as a stimulation technique in both carbonate and sandstone reservoirs. Unlike hydraulic fracturing, matrix acidizing is strongly affected by the reaction process of acid and rock (Li and Horne, 2009), during which time reactive minerals are dissolved by the acid.

The acid rock reaction is actually a type of liquid–solid heterogeneous non-catalytic reaction, which is usually defined by the shrinking core model introduced by Yagi and Kunii (1955). By assuming that fluid enters the interior of large particles along the pores and reacts with small particles, Sohn and Szekely (1972) viewed a large-size particle as a composite of small equally sized particles; however, they did not consider surface roughness or the size distribution of the particles in their model. Although Zhongwei et al. (1996) did consider the particle size heterogeneity, they ignored the surface roughness of the particles. In another study, and based on the model of Sohn & Szekely, fractal theory was applied to describe the surface roughness, but the distribution of the particle size was not considered (Ying et al., 2003).

On the microscopic scale, it is observed that the interface of the acid–rock reaction is rough with fractal character (Farin and Avnir, 1987; Li-Ming and Shu-Quan, 1993). Recently, fractal character has been observed in reservoir development studies, including the process of matrix acidizing. Li and Horne (2009) applied a fractal technique to characterize the heterogeneity between Geysers rock and Berea sandstone. Izgec et al. (2010) investigated the effect of heterogeneity on the acidization

of vuggy carbonate using high resolution computerized tomography imagery, geo-statistical characterization, acid core-flood experiments and numerical simulations. Based on the shrinking core model and fractal theory, Li et al. (2010) established a fractal model for single rough limestone particle corrosion by hydrochloric acid.

The above reviews indicate that there are not yet any comprehensive studies that investigate the influence of both surface roughness and the size distribution of mineral particles on the acid rock reaction.

To overcome this omission, we first consider a piece of rock as a cluster of rough and hetero-granular mineral particles. Then, we describe the structure of the cluster by a fractal methodology and attempt to rationalize the cluster etch model based on an analysis of the reaction and the traditionally used shrinking core model. Finally, we perform a sensitivity analysis of the model to determine the influence of the model parameters on the etching behavior.

### 1.1. Structure of the mineral particle cluster and its dissolution

We consider the mineral particles as rough surfaces of different sizes and simplify the cubic porous structure of a particle cluster, as shown in Fig. 1. The gray part of Fig. 1 represents the rough external surface of a particle cluster. Because both the external surface of the cluster and the single particle are similar, we can consider that they have the same fractal dimension. In addition, intergranular fractures (black lines in Fig. 1) and intergranular pores (the two blue areas of the inner particle cluster in Fig. 1) are formed when the particles come in contact. The larger blue area in Fig. 1 represents an intragranular pore that has been shaped after being dissolved by acid. A cumulative distribution function,  $F(r)$ , is introduced to describe the diverse size of the particles,

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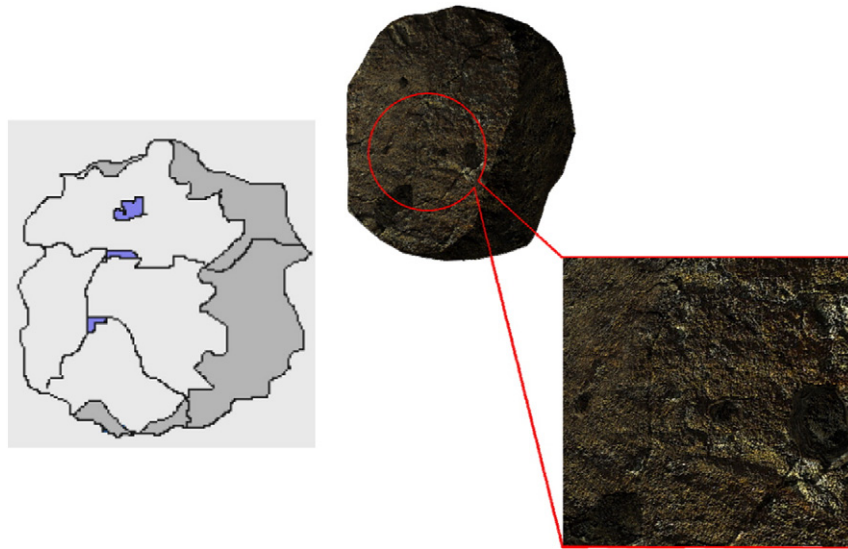


Fig. 1. Cross section of a particle cluster.

and its corresponding probability density function is presented, where  $r$  is the equivalent radius of the particles.

Fig. 2 shows the size variation of a single particle within the cluster during the reaction. Here,  $r_0$  represents the initial equivalent radius and  $r$  represents the equivalent radius after reaction time  $t$ . During the reaction process, hydrogen ions in the acid not only react with the grains of the outside surface particles but also every single particle they contact while entering the inner particle cluster through intergranular pores or fractures. Thus, the acidizing process can be regarded as an accumulation of the single particle corrosion process.

In fractal theory, the relationship between the external surface area of a particle and its radius can be expressed as:

$$S = C_1 r^D \tag{1}$$

where  $S$  is the surface area of the solid particle,  $C_1$  is the shape coefficient of the surface fractal,  $D$  is the fractal dimension of the particle external surface,  $D \in [2, 3]$ , and  $r$  refers to the equivalent radii of the particles. For spherical particles, the values of  $D$  and  $C_1$  are 2 and  $4\pi$ , respectively, and  $S$  equals  $4\pi r^2$ .

According to the correlation given by Mandelbrot of the surface area of solid particle  $S$  with its volume  $V$ ,

$$S^{\frac{3}{D}} = K_1 r^{\frac{2-D}{D}} V^{\frac{1}{D}} \tag{2}$$

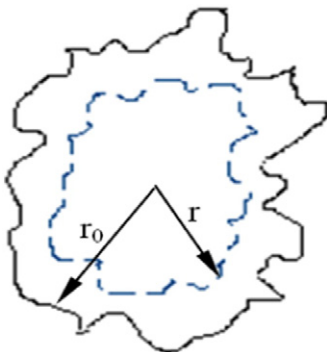


Fig. 2. Size change of a single particle following its reaction with acid.

the equation for the particle volume can be expressed as:

$$V = C_2 r^{4-\frac{2}{D}} \tag{3}$$

where  $C_2$  is a constant and independent of the particle radius,  $C_2 = C_1^{\frac{3}{D}} / K_1$ . For spherical particles,  $D = 2$ ,  $C_2 = \frac{4\pi}{3}$ , and  $V = \frac{4\pi}{3} r^3$ .

During the reaction, the volume of the particles will be reduced gradually with consequent changes to the surface shape and its fractal dimension. Qu et al. (1992) found that the fractal dimension changes rapidly in the initial stages of the reaction. However, it tends to stabilize immediately following the initial transition phase. Thus, we assume that the fractal dimension of the particle external surface is a constant during the entire dissolution process of a mineral cluster.

### 1.2. Modified shrinking core model

Generally, the acid–rock reaction rate is influenced at several stages, including the transfer, absorption and reaction of hydrogen ions on the particle surface. It is clear that the slowest step will be the rate-limiting step.

Regarding matrix acidizing, the reaction between limestone and hydrochloric acid is primarily controlled at the hydrogen ion transport stage. However, other acid–rock reactions are controlled at the surface reaction stage, such as the reaction between dolomite and hydrochloric acid at a low temperature and the reaction between hydrofluoric acid and sandstone (including quartz, potassium feldspar, soda feldspar, etc.). In this paper, we mainly focus on the general reaction rate of acid rock that is controlled at the surface reaction stage.

## 2. A model for particle cluster dissolution that is controlled by a surface reaction

### 2.1. The model for a single particle

The equation of the surface reaction rate for a single particle, which is characterized by the mineral consumption rate, can be expressed in general terms as a rate equation in a power function form: (Gantang, 1990)

$$r_m = K_m C_m^p C_{H^+}^q \tag{4}$$

In Eq. (4),  $K_m$  is the rate constant of the chemical reaction (in units of  $(\text{mol}/\text{m}^3)^{1-(p+q)} \cdot \text{s}^{-1}$ ),  $C_m$  is the concentration of calcium carbonate in

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