

TABLE III-continued

Solubility of CaCO ₃ Under Varying Temperature and Pressure	
Temperature (F.)	Half-life (weeks)
500	13
600	7
700	5

At temperatures above about 500° F., the calcium carbonate will degrade relatively substantially while at lower temperatures (e.g. less than about 400° F.) the calcium carbonate remains relatively stable for typical stimulation times of several weeks.

Silicon dioxide dissolves congruently in pure water to produce silicic acid. In pure water the solubility rate of silicon dioxide is dependent on the nature of the silicon oxide phase: amorphous silicon dioxide dissolves faster than cristobalite which is, in turn, dissolves faster than quartz. Table IV outlines dissolution for silicon dioxide at various temperatures.

TABLE IV

Half-Lives for Dissolution of Amorphous Silica and Quartz		
Temperature (F.)	Amorphous Silicon Dioxide Half Life (weeks)	Quartz Half Life (weeks)
100	97767	5071696
200	2357	82198
300	148	3728
400	18.2	349
500	3.64	55.3
600	0.98	12.1
700	0.34	3.51

Notably, silicon dioxide has a very high stability up to temperatures above about 500° F. (amorphous silicon dioxide) and 600° F. (quartz). Additional degradation aids can optionally be used to accelerate degradation of these materials. For example, sodium hydroxide, potassium hydroxide, or the like can dissolve silicon dioxide. Optionally, a mixture of ethylene glycol, triethanolamine, and sodium hydroxide can be used to form silatrane glycol which is sufficiently stable to allow simple removal from the fractures.

A magnesium ammonium phosphate cement may be synthesized using 30.4 parts ammonium dihydrogen phosphate, 40.2 parts of magnesium oxide, and 29.4 parts water. The solids may be added to the water and stirred in to give a paste that set to a hard solid in 3 minutes. This cement consists of struvite, NH₄MgPO₄·6H₂O, usually accompanied by schertelite, (NH₄)₂Mg(HPO₄)₂·4H₂O and traces of dittmarite, NH₄MgPO₄·H₂O, and/or stercorite, NaNH₄HPO₄·4H₂O. The cement may be aged for 24 hours and then lightly ground. A portion of the resulting powder is heated in a bath of deionized water at 170° F. After 3.5 days the cement may lose 8.2% by weight.

A magnesium potassium phosphate cement may be prepared in the same manner as the magnesium ammonium phosphate cement by replacing the ammonium dihydrogen phosphate with an equimolar amount of potassium dihydrogen phosphate and additional water (23.6 parts potassium dihydrogen phosphate, 26.7 parts of magnesium oxide, and 49.7 parts water). The solids may be added to the water and stirred in to give a paste that sets to a hard solid in 10 minutes. This cementing phase present is mainly KMg(PO₄)₂·6H₂O. A portion of the resulting powder was heated in a bath of deionized water at 170° F. After 3.5 days the cement may lose 31.5% by weight.

A different magnesium oxyphosphate cement, MgHPO₄·3H₂O can be produced from magnesium oxide and aqueous phosphoric acid as the acid source. This mineral may be obtained from a commercial source. A portion of the resulting powder may be heated in a bath of deionized water at 170° F. After 3.5 days the cement may gain 23.8% by weight. A hydrated phase may be formed, such as MgHPO₄·3H₂O.

The foregoing detailed description describes the invention with reference to specific exemplary embodiments. However, it will be appreciated that various modifications and changes can be made without departing from the scope of the present invention as set forth in the appended claims. The detailed description and accompanying drawings are to be regarded as merely illustrative, rather than as restrictive, and all such modifications or changes, if any, are intended to fall within the scope of the present invention as described and set forth herein.

What is claimed is:

1. A method of hydraulic stimulation in underground reservoir formations, comprising:

introducing a particulate diverting agent into a first fracture within an underground reservoir formation sufficient to at least partially hydraulically isolate the first fracture, the particulate diverting agent being a temporary material which substantially degrades over an extended time upon exposure to heat at a degradation temperature;

stimulating the underground reservoir formation with a stimulation fluid at a temperature below the degradation temperature sufficient to expand a second fracture within the underground reservoir formation; and

allowing the particulate diverting agent to substantially degrade by reducing flow of the stimulation fluid to allow native heat within the underground reservoir formation to heat the particulate diverting agent to the degradation temperature.

2. The method of claim 1, wherein the particulate diverting agent is selected from the group consisting of polymer, glass, acid-base cement and combinations thereof.

3. The method of claim 2, wherein the particulate diverting agent is a polyester selected from the group consisting of polyethylene terephthalate (PET), polybutylene succinate (PBS), polycaprolactone (PCL), polypropylene fumarate (PPF), polyhydroxyalkanoates (PHA), and combinations thereof.

4. The method of claim 2, wherein the particulate diverting agent is a thermoset polymer selected from the group consisting of thermoset phenol formaldehyde resin, polyether ether ketone (PEEK), and combinations thereof.

5. The method of claim 2, wherein the particulate diverting agent is a polycarbonate, rayon, polyvinyl alcohol, polyglycolic acid, and combinations thereof.

6. The method of claim 5, wherein the particulate diverting agent is a polycarbonate including at least one of polybisphenyl carbonate and polypropylene carbonate.

7. The method of claim 2, wherein the particulate diverting agent is a polyaramid.

8. The method of claim 2, wherein the particulate diverting agent is at least one of poly(isophthaloyl chloride/m-phenylenediamine) (NOMEX) and poly-paraphenylene terephthalamide (KEVLAR).

9. The method of claim 2, wherein the particulate diverting agent is calcium carbonate.

10. The method of claim 2, wherein the particulate diverting agent is amorphous or crystalline silicon dioxide.