



Developing high performance phosphogypsum-based cementitious materials for oil-well cementing through a step-by-step optimization method



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ARTICLE INFO

Article history:

Received 12 November 2015

Received in revised form

8 May 2016

Accepted 21 May 2016

Available online 29 June 2016

Keywords:

Oil-well cementing

Cementitious material

Phosphogypsum

Linear expansion

Low permeability

ABSTRACT

In the present study, unprocessed phosphogypsum (PG), a byproduct generated by the phosphorus fertilizer industry, is mixed with conventional oil-well cement (CM) and ground-granulated blast-furnace slag (GGBFS or SG), along with other activators and admixtures (such as silica fume (SF), retarder (USZ), and fluid loss control additive (BXF200-L)), to form a PGS slurry for oil well cementing. The mix proportion was optimized step-by-step according to the key properties of hardened PGS slurry, such as compressive strength, linear expansion, porosity, and permeability. The results indicate that the optimized PGS slurry (PGS-optimal slurry), made with the neat PGS:SF:USZ:BXF200-L (by weight) = 100:6:0.4:2, $w/c = 0.44$, where the neat PGS is consisting of a ratio of PG:SG:CM = 50:20:30 (by weight), had met major technical requirements for oil well cementing operation. Advantageous over the hardened CM slurry, the hardened PGS-optimal slurry generates significant expansion during hydration, thus providing the hardened slurry with excellent shrinkage compensation capability. The hardened PGS-optimal slurry has lower porosity, especially lower amount of harmful pores (>100 nm), than the hardened CM slurry. Consequently, the hardened PGS-optimal slurry also displays much lower permeability.

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1. Introduction

Phosphogypsum (PG) is a byproduct generated by the phosphorus fertilizer industry. It consists of mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and some impurities (such as P_2O_5 , fluorides, organic substance, and alkali metals). Currently, the annual PG production worldwide is about 160 million tons, of which 40 million tons are produced in the United States and 50 million tons in China. According to the International Atomic Energy Agency (IAEA 2013) [1], “while the use of phosphogypsum continues in several parts of the world, concerns about its radioactivity content and, to a lesser extent, its heavy metals content, have led to restrictions on the use of phosphogypsum in some markets, even though such concerns do not always have a proper scientific foundation. This has resulted in phosphogypsum stacks being, in effect, turned from short term holding piles into long term disposal facilities.” As a result, there are great

urgencies, demands and interests to recycle the PG and to minimize its negative impacts on the environment [2–6].

In addition to being utilized in agriculture [7], PG is also increasingly used by the cement industry and other building material manufacturers [8–10]. Yang used PG as raw material for preparation of non-autoclaved aerated concrete, and the optimal mix proportion was found: cement 15%, GGBFS 30%, PG 55%, quick lime 7%, Na_2SO_4 1.6%, Al powder 0.074%, W/S 0.45 [11]. Degirmenci used PG for soil stabilization of roadbed materials [12]. Lima incorporated PG as an alternative raw material for Portland cement production [13]. Zhou developed non-fired bricks by using PG [14].

Recently, some researchers have explored a PG-based cementitious system (PGS) consisting of mainly PG, together with appropriate amounts of fly-ash (FA), slag (SG), lime and/or silica fume (SF), as activators, and they found that the hydrated PGS generally has good compressive strength and water resistance [15–17]. The research has indicated that during the applications where PG is subjected to chemical, physical, and/or thermal treatments, much of the harmful components in the PG may be decomposed, and the new products (e. g., PGS) can sequester the PG

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Table 1
Physical properties of raw materials used (%).

Raw material	Appearance	Color	Specific gravity/g/cm ³	Specific area m ² /Kg
PG	Power	Grey	2.35	350
SG	Power	Grey	2.92	410
SF	Power	Grey	2.20	434
CM	Power	Grey	3.12	290

impurities and decrease the degree of its negative impacts [18,19].

Lately, PGS has been introduced into oil well construction in China due to its desirable performance at high temperature and pressure; however, little research has been reported on such a PGS application. In the oil well cementing process, a slurry is pumped into a casing. At the end of the casing, the slurry is pushed out to flow up to the surface of the earth, forming a layer in the spaces between the casing and wellbore (called annulus of oil-well), which supports the casing, separates the drilling oil or gas from ground water and other liquids, and prevents the migration of hydrocarbons from one ground layer to another [20]. The poor cementing performance of the slurry (such as not being able to fill the entire annulus due to poor flowability and fluid loss due to water-solid segregation and/or due to the water forced out from the slurry as the slurry passes through a restricted/narrow area) can result in a weak insulation, jeopardize the oil/gas production safety, and decrease the exploitation life and the output of oil and gas wells. To obtain desirable cementing performance, the slurry must have good engineering properties (such as fluidity, filtrate loss, setting time, and thickening time). The hardened slurry, called cement sheath, must have good mechanical properties and low shrinkage behavior so as to prevent cross flow of fluid and gas from gap of cement-formation interface and cement-casing interface, and potential cracking of cement sheath.

Much effort has been made on designing and processing oil well cement-based materials to meet increasing demands for better performance, among which the most effective ways are optimization of mix proportion and use of admixtures and/or additives. For example, surfactants are used in oil well cement as retarding agent, dispersing agent, and forming agent. Supplementary cementitious materials (SCMs), such as fly-ash, slag, and silica fume (SF), have been increasingly used in oil well cement slurry for various benefits, including waste material utilization, cost reduction, fresh and hardened slurry property improvement [21,22]. To increase mechanical properties and cracking resistance, and decrease shrinkage of cement sheath, the D.S. petroleum and Halliburton petroleum company developed a latex slurry in 1980s [23]. Then Halliburton and Schlumberger petroleum company successfully used special fibers to oil-field of North American and Middle East [24,25]. BJ Services developed cement, called crosslink cement that exhibited excellent thixotropy under 120 °C [26]. To prevent fluid loss or filtration control, Gu et al. developed the super low density foam slurry with density less than 1.0 g/cm³.

Shrinkage of oil well cement slurry can impair the bond between casing cement and cement-formation and result in loss of zonal insulation. There are several types of shrinkage occurring in oil well cement slurry: dehydration shrinkage, chemical shrinkage, and auto-generous shrinkage. Dehydration shrinkage occurs due to water expulsion when the oil well cement is still in a liquid-like or early-set state [27]. Chemical shrinkage occurs during initial stage of cement hydration stage, as the hydration reaction products occupy less volume than the original paste. Auto-generous shrinkage occurs after cement slurry start setting and during hardening. Expansion agents are often added into oil well cement to produce a pre-stress that compensate the stress induced by shrinkage [28].

PGS hydration products consisted of mainly PG (CaSO₄ · 2H₂O), CSH, ettringite (AFt) and AFm phase [29]. The ettringite formation is accompanied by a large volume expansion. In the oil field application, such an expansion is restrained by the zonal isolation, thus building an internal stress in the material during the slag hydration. This prestress can compensate the stress induced by shrinkage after the material is hardened.

The purpose of the present study is to extend the use of PG in construction materials so as to reduce the long-term, irreversible negative impacts of PG stacking. This study is specifically aimed at developing a systematical method for designing phosphogypsum-based cementitious materials with various activators, additives, and admixtures for oil well cementing. In the present study, unprocessed PG was used together with different activators (such as oil-well cement (CM), and slag (SG)), additives (lime and silica fume (SF)), and other admixtures (retarder and filtration control agent). A step-by-step mix design method was employed to select a basic PGS mix and then to optimize the amount of each of the additives and admixtures to be used based on the strength and workability requirements for oil well cementing. In addition to strength and flowability, volume stability, permeability, porosity and micro-structure of the finally selected PGS slurry were evaluated, and their effects on shrinkage cracking resistance of cement sheath were analyzed.

2. Experimental

2.1. Materials

The materials used in the present study include PG, ground-granulated blast-furnace slag (GGBFS, or SG), silica fume (SF), lime, retarder, fluid loss control additive, G-grade oil-well cement (CM) and a defoaming agent. PG, SG and CM are used as major cementitious materials; SF is as an additive; and lime is an activator; Table 1 shows the main physical property of PG, SG, SF and CM.

Table 2 gives the main chemical compositions of PG, SG and SF as determined by X-ray fluorescence (XRF). The lime used had CaO content >90%. The retarder used (named USZ) is an aliphatic compound (powder). Fluid loss control additive (named BXF200-L) is a copolymer of acrylamide (AM) and 2-acrylamide base-2-methyl sulfonic acid (AMPS). The defoamer is tributyl phosphate.

Fig. 1 displays the micromorphology of the raw PG observed under a scanning electron microscope (SEM), where the raw PG was ground to pass a 120 μm sieve. The platelike crystals were observed from the PG sample. Fig. 1 displays the X-ray diffraction

Table 2
Chemical composition of raw materials used (%).

Material	CaO	SO ₃	SiO ₂	Al ₂ O ₃	P ₂ O ₅	K ₂ O	TiO ₂	MgO	MnO
PG	30.85	31.85	4.65	4.20	3.22	0.32	0.2	0.24	–
SG	31.75	–	36.86	19.84	–	0.90	1.13	8.54	0.24
SF	1.45	–	92.34	0.25	0.28	–	–	0.41	–
CM	67.77	1.67	22.43	4.76	–	–	–	1.14	–

Notes: loss on ignition of PG is 22.94%.

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