

# 纳米二氧化硅在固井水泥浆中的应用研究进展

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**摘要:**近年来,纳米二氧化硅由于其本身超高的比表面积及与水泥的火山灰反应,在石油天然气工业中引起了广泛的关注。本文系统梳理了纳米二氧化硅在固井水泥浆中的研究现状,着重介绍了纳米二氧化硅对固井水泥浆的失水量和稠化时间、对水泥石的力学性能和微观结构的影响,总结了纳米二氧化硅在高温条件下的性能表现,探讨了纳米二氧化硅在固井水泥浆的应用中存在的问题、面临的挑战以及未来的发展方向,以期对纳米二氧化硅在固井领域的应用和发展有所帮助。

**关键词:**固井水泥浆;纳米二氧化硅;微结构;综合性能;油气井固井

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## Research status of nano-silica application in well cementing slurry

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**Abstract:** In recent years, nano-silica has attracted extensive attention in the oil and gas industry due to its ultra-high specific surface area and pozzolanic reaction with cement. In this paper, the research status of nano-silica in cementing slurry is systematically reviewed with focus on the effects of nano-silica on the water loss and thickening time of cementing slurry, and on mechanical properties and microstructure of hardened cementing slurry as well. The effects of nano-silica on the performance of cementing slurry under high temperature is also summarized. The existing problems, challenges and future development direction of nano-silica application in cementing slurry are discussed so as to provide some suggestions and ideas for the development and application of nano-silica in the cementing field.

**Key words:** cementing slurry; nano-silica; microstructure; compressive strength; oil and gas well cementing

## 0 引言

固井是油气井建井过程中不可或缺的一个重要环节<sup>[1-3]</sup>,具有支撑套管、封闭地下复杂地层、防止层

系串通和保护产层的重要作用<sup>[4-5]</sup>。随着油气资源勘探开发的不断深入,开采难度逐渐增加。为了保障油气资源安全、可靠、高效、经济地产出,对于固井质量

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的要求也随之提高<sup>[1,5-7]</sup>。如何有效提高固井水泥浆和地层之间的界面胶结强度对于提高固井质量和确保油气井功能完整性显得尤为重要。为此,研究人员开始向水泥浆中添加纳米材料以改善水泥浆的综合性能,延长油气井服役寿命,并由此减少与改造相关或由于水泥环和套管故障而造成的技术损失。

自20世纪80年代以来,纳米技术因其特殊效应在国内外都引起了广泛的关注,并得以迅速发展,同时使得很多工业领域发生了革命性的变化<sup>[8-19]</sup>。在石油天然气工业中,纳米材料已在勘探开发中得到了广泛的应用<sup>[9-10,14]</sup>。近年来,纳米二氧化硅(nano silica,以下简称NS)逐渐被引入固井水泥浆中,并取得了较好的效果。通过在水泥基材料中加入NS,可以赋予水泥浆新的功能<sup>[20-22]</sup>。

Qing等<sup>[23-34]</sup>研究认为,NS是水泥水化的最佳促进剂。在水泥浆中添加NS纳米颗粒可以加速水泥浆的水化进程,缩短水泥浆候凝时间,节省钻机空闲时间,从而有效节约钻井综合成本<sup>[16,22,34-37]</sup>。由于NS的高比表面积和纳米级尺寸效应,可填充在水泥石的微纳孔隙内,同时还可以充当水化产物的成核位点。此外,由于NS的火山灰效应,可与水泥水化产生的氢氧化钙(calcium hydroxide, CH)发生水化反应,从而对水泥浆水化放热、稠化时间、强度发展和结构变化等产生一定影响。

目前,NS在固井水泥浆中的研究与应用日益增多。然而,与之相关的系统报导却相对较少。因此,本文综述了NS在固井领域的研究及应用进展,重点介绍了NS对水泥浆失水量、稠化时间、力学性能和微观结构等的影响,总结了NS在高温条件下的性能表现,探讨了NS在固井水泥浆的应用中所存在的问题、面临的挑战以及未来的发展方向,以期对纳米技术在固井领域的应用和发展有所帮助。

## 1 纳米二氧化硅及其对水泥浆性能的影响

NS是一种由极细的二氧化硅玻璃颗粒组成的高效火山灰材料,化学式为SiO<sub>2</sub>,外观为白色粉末,颗粒直径一般为1~100 nm。

NS对水泥浆体的影响是多方面的<sup>[38-39]</sup>。大多数学者报导了NS对固井水泥浆性能的积极作用,如图1所示。NS不仅可以填充在水泥颗粒之间的空隙中,为水泥水化提供成核位置<sup>[34,40-41]</sup>、产生填充效应<sup>[41]</sup>、增加水泥石的密度<sup>[26]</sup>,还可以促进水泥石早期力学强度

的发展<sup>[23-24,42-44]</sup>。由于其自身的高比表面积,所以会对水泥浆的失水量和稠化时间产生影响。由于其火山灰效应,可以促进水泥水化,提高水泥石的抗压强度,还可以降低水泥石的孔隙率和提高水泥石的抗渗性能,细化微孔隙结构,增强水泥石的耐久性等。

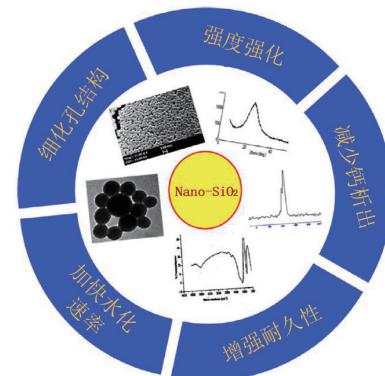


图1 NS对固井水泥浆性能的积极作用<sup>[39]</sup>

Fig.1 Positive effect of NS on the properties of cementing slurry

### 1.1 对失水量的影响

在固井作业中,失水会对水泥浆的性能产生非常不利的影响,严重可能导致固井失效。研究者们普遍认为,缺乏降滤失控制是导致固井失效的主要原因。常见的方法是向水泥浆中加入化学添加剂,以降低水泥浆滤失量,减少流体向地层的漏失。

Diasty等<sup>[9,11,16,45-46]</sup>认为,将NS加入水泥浆中用作液体损失控制剂时,可有效控制的流体损失,抵抗气体迁移。Ershadi等<sup>[21]</sup>研究了不同掺量的NS对水泥浆失水量的影响,并对其影响机理进行了分析,发现掺1% NS的水泥浆较未掺NS的水泥浆的失水量相对减少了43%。随NS掺量的增加,水泥浆的滤失量会逐渐减小。Ershadi等<sup>[21]</sup>认为,NS颗粒可以填充在水泥基质的孔隙之间,堵塞水泥颗粒之间的开口,阻止水泥浆中的液体与固体分离,提高水泥浆的保水性。

### 1.2 对稠化时间的影响

水泥浆稠化时间是水泥浆的可泵送时间或开始稠化所需的时间<sup>[47]</sup>。在深水井和超深井的建井过程中,建井成本往往非常高昂。为此,国内外研究者们都极力寻找有效的方法以实现低成本且最大限度地从深层和超深储层中钻采油气资源。水泥浆稠化时间基本上是水泥凝固所需的时间。正是在这段时间里,钻机闲置,钻机成本增加。在固井作业

中,缩短水泥浆的候凝时间往往意味着减少了固井时间,从而节省了占用钻机时间和成本。为此,有必要缩短水泥浆的稠化时间以节约钻井成本。

而通过向水浆中加入NS则可以有效缩短水泥浆稠化时间。NS巨大的比表面积和火山灰活性正是导致水泥浆凝结时间缩短的主要原因。NS可与水泥水化产生的CH发生水化反应,促进水化反应的进行,从而缩短水泥浆的凝结时间<sup>[28,48]</sup>。

一般认为,通过向水泥浆中添加1%~2% (BWOC) 的NS可以获得较为理想的稠化时间<sup>[21,49]</sup>。Quercia等<sup>[50]</sup>通过向常规G级油井水泥浆中添加1%的NS,将稠化时间缩短了151 min。Ershadi等<sup>[21]</sup>发现在水泥浆中掺入1%的NS可将稠化时间从8 h减少到2 h以下,掺3% NS的水泥浆的稠化时间较2% NS的水泥浆缩短了24.7%。Senff等<sup>[51]</sup>将1.0%、1.5%、2.0%和2.5%的无定形NS掺入水泥浆中,发现水泥浆的初凝时间和终凝时间都随NS的掺入而缩短了。NS掺量越高,凝结时间越短。Chithra等<sup>[49]</sup>也探究了不同掺量NS对水泥浆初凝时间和终凝时间的影响,如图2所示。由图2可知,随NS掺量的增加,水泥浆初凝时间和终凝时间都逐渐减小,但初凝时间随NS掺量的增加整体减少趋势不大,而终凝时间随NS掺量的增加降低幅度明显大于初凝时间的降低幅度。

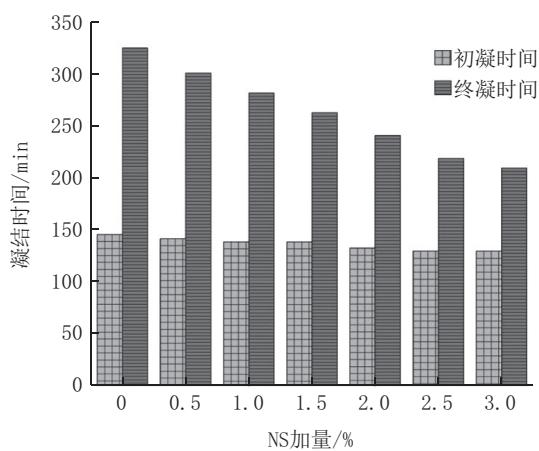


图2 不同含量NS对水泥浆凝固时间的影响<sup>[49]</sup>

Fig.2 Effect of NS adding amount on the setting time of cement samples

由此,可以得出NS的掺入可以有效降低水泥浆的稠化时间,且掺量越高,稠化时间越短。相比于初凝时间,终凝时间对NS掺量的变化往往更为敏感。

### 1.3 对力学性能的影响

通常,与其他力学性能相比,学者们往往更加注重对水泥石抗压强度的研究。在研究NS对水泥石抗压强度的影响方面,国内外学者作了大量的研究工作。大量文献<sup>[31,52~60]</sup>报道了NS对水泥石抗压强度的促进作用,认为在水泥浆中加入NS后,水泥浆的抗压强度可以大幅度提高。Wang等<sup>[34]</sup>认为,NS对水泥石的增强效应主要归因于两个因素:(1)填充作用改善微观结构,使水泥石微结构更为致密;(2)作为促进火山灰反应的活化剂。

Hasan等<sup>[54]</sup>发现,相比于水泥净浆、掺粉煤灰和掺硅灰的水泥浆,掺NS的水泥浆具有较高的抗压强度。Jo等<sup>[55]</sup>发现,掺有10% NS的水泥石的抗压强度是空白对照样品的3倍。Haruehansapong等<sup>[61]</sup>认为,NS颗粒的最佳用量为9%。Ershadi等<sup>[21]</sup>对比了掺有0%、1%和1.5% NS的水泥浆的抗压强度,发现掺1% NS的水泥浆相较于未掺NS的水泥浆的抗压强度提高了100%,而掺1.5% NS的水泥浆与掺1% NS的水泥浆相比,抗压强度反而降低了7%,但是都高于未掺NS的对照组。

针对不同掺量NS对水泥浆抗压强度的影响,Chithra等<sup>[49]</sup>做了更为深入细致的实验研究,他们采用0.5%、1%、1.5%、2%、2.5%和3%的NS(粒径5~40 nm)取代硅酸盐水泥,测试了硬化水泥浆体在3、7、28、56和90 d 5个不同龄期的抗压强度(见图3)。由图3可知,所有掺加了NS的样品在3、7、28、56和90 d的抗压强度均高于未掺NS的对照样品。当NS的掺量≤2%时,随NS掺量的增加,水泥试样的抗压强度越高;当掺量>2%时,水泥试样的抗压强度随NS掺量的增加而减少,但仍高于未掺NS的试样。

与此同时,不同粒径的NS也会表现出不同的强度增强效应。Haruehansapong等<sup>[61]</sup>研究了粒径分别为12、20、40 nm的NS对水泥浆的抗压强度的影响,发现NS的加入显著提高了水泥浆的抗压强度,与12和20 nm的NS相比,掺40 nm NS的水泥浆具有相对更高的抗压强度。Haruehansapong等<sup>[61]</sup>分析认为,粒度更小的NS颗粒更容易出现团聚,纳米颗粒无法得到有效分散,从而导致其强度低。

由Ershadi等<sup>[21]</sup>和Chithra等<sup>[49]</sup>的研究结果可以初步得出如下结论,NS具有增强效果,但是NS的掺量并不是越高越好。那么,NS的最佳掺量是多少呢?对于不同的水泥浆体系,结论并不完全一

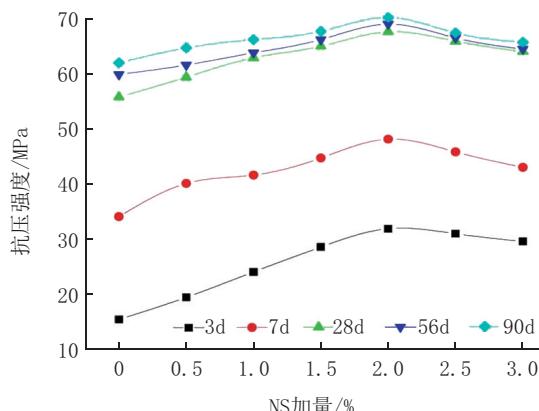


图3 不同掺量NS对水泥样品抗压强度的影响<sup>[49]</sup>

Fig.3 Effect of NS adding amount on the compressive strength of cement samples

致。Haruehansapong 等<sup>[61]</sup>认为,NS 的粒径只影响水泥浆的抗压强度,而对最佳取代量没有影响。就提高水泥石的抗压强度而言,NS的最佳掺量应该处在1%~10%(BWOC)之间。

#### 1.4 对微观结构的影响

将NS添加到水泥浆中会影响水泥石的微观结构,对水泥石的孔隙率、渗透率和水泥环的防窜性能产生一定影响。Ershadi等<sup>[21]</sup>发现,随NS的掺入,水泥石的孔隙率和渗透率均出现一定程度的下降。相较于未掺NS的空白组,掺1%NS的水泥石的孔隙率和渗透率分别降低了33%和99%;当NS的掺量超过1%时,在水泥浆中加入更多的NS并不能有效地改变水泥浆的渗透率和孔隙率。Jo等<sup>[55]</sup>将质量分数为3%、6%、10%和12%的无定形NS与水泥混合,发现掺有10%NS的硬化水泥浆体在7 d水化龄期的CH含量为4.06%,而未掺NS的空白组中剩余的CH含量为8.89%。

由于NS的火山灰活性,可以消耗水泥水化产生的CH,形成额外的C—S—H凝胶,并促进水泥石的致密化和改善水泥石的微观结构<sup>[11,23,30,48,55,62-64]</sup>。同时,由于NS的填充效应<sup>[65]</sup>,NS颗粒填充在水泥基体的空隙内,硬化水泥浆体的孔隙率和渗透率得以降低,水泥石的微观结构随之发生显著改变,从而形成更加紧密的结构<sup>[25,45,66]</sup>,并可有效降低水泥环空内发生窜槽和气体运移的可能性<sup>[21]</sup>。

## 2 纳米二氧化硅在高温条件下的应用

随着常规石油天然气的大量开采和快速消耗,

非常规油气的勘探与开发逐渐提上了日程。由于遇到高温高压,非常规油气开采的难度和风险增大,与之配套的固井难度也相应增加。高温的存在促使水泥浆提早凝固,容易使水泥凝结不当,并可能导致水泥内部出现裂缝<sup>[67]</sup>。严重可能引发流体迁移、窜槽,导致补注水泥浆,从而进一步增加成本。通过在水泥浆中加入NS,可以有效缓解水泥浆内的窜槽现象,提高油井的完整性和耐久性。

然而,目前关于NS对油井水泥的改性的研究大多数都集中在正常固化温度(20~80 °C)下,对于高温条件下的改性研究却相对较少。在110 °C以上,C—S—H凝胶会转变为水合硅酸二钙(C<sub>2</sub>—S—H),从而导致强度损失<sup>[34]</sup>。为了防止强度衰退,必须提高二氧化硅在水泥浆中的比例,以降低水泥浆中的总石灰与二氧化硅的比例,即降低Ca/Si比。

针对高温水泥环力学性能强度衰退这一问题。何毅等<sup>[68]</sup>制备了NS与胶乳的复合乳液,发现NS可以提高胶乳水泥浆在高温下的稳定性。高元等<sup>[69]</sup>针对顺南区块超深气井高温高压情况,将纳米硅乳液与胶乳复配制得一种新型防气窜水泥浆体系,在顺南5-2井和顺南6井中得到了成功应用。刘慧婷等<sup>[70]</sup>针对固井水泥浆强度发展慢等问题,研制了一种纳米硅溶胶,在大港油田10余口油层套管固井中的应用效果良好。Wang等<sup>[34]</sup>研究了在150 °C/65 MPa的条件下分别将0%、4%、6%的NS与35%的硅粉掺入水泥浆中,发现在28 d水化龄期时,仅含有35%硅粉的样品的抗压强度为52.38 MPa,而额外添加了4%和6%的NS的样品的强度分别提高到了63.86和64.16 MPa。说明在高温下,NS可以有效防止油井水泥在高温下的强度衰退。

## 3 纳米二氧化硅在水泥浆中的应用问题探讨

NS与其他油井水泥添加剂有较好的配伍性。通过将NS掺入水泥浆中,可以激活水泥的火山灰反应,形成更加致密的微观结构,从而可以提高水泥石的力学性能,降低孔隙率和渗透率,提高油气井的耐久性和服役寿命等。NS不仅可以缩短水泥浆在低温条件下的稠化时间,还可以有效防止油井水泥在高温下的强度衰退。

然而,如果NS颗粒在水泥浆中不能够得到均匀分散,往往会造成空隙和薄弱区域<sup>[57]</sup>。NS会增加水泥浆的粘度,导致泵送能力和空气夹带问题。与此同

时,不同粒径、不同状态的NS也会表现出不同的强度增强效应,哪种粒径最优、哪种状态的NS性能最好,都值得进一步的探讨。此外,NS在固井水泥浆应用过程中还面临着另一个亟待解决的问题,即难以确定水泥浆中应添加多少NS才能获得最佳性能<sup>[7]</sup>。

一些学者认为,为避免NS在混合浆料时出现团聚现象,比较合适的NS加量为1%~5%。而Hasan等<sup>[54]</sup>则认为,如果NS可以得到有效的分散,其加量可增加至10%。Singh等<sup>[63]</sup>认为,NS的最佳掺量取决于多种因素,如NS的类型(干粉或胶体)。Hasan等<sup>[54]</sup>认为,在早期水化龄期时,在水泥中掺入相同质量的胶体NS比粉末NS具有更高的抗压强度;而在水化后期,胶体NS会表现出和粉末NS相同的抗压强度。

#### 4 结论与展望

NS在固井水泥浆中具有很大的应用价值。通过在水泥浆中掺入NS可有效缩短水泥浆候凝时间、减少失水量,提高水泥石的抗压强度,改善微观结构,提高储层封固完整性和延长油气井服役寿命,保障生产过程中的人员安全。同时,NS可防止油井水泥在高温下的强度衰退,有助于降低油气田开发总成本。NS在改善固井质量、提高水泥石强度、保持井筒完整性等方面起重要的作用。结合国内外NS在固井水泥浆的应用研究现状,还存在如下几个问题:

(1)NS由于其高比表面积而难以均匀地分散在水泥浆中,如何更加有效地分散NS值得进一步探究。考虑通过表面改性、改变生产工艺、复配分散剂等方式来实现NS的有效分散。

(2)是否有最佳NS掺量? NS的类型(干粉或胶体)、尺寸(粒度分布范围和平均尺寸)和表面特性等是否会对最佳NS掺量产生影响仍需进一步探究。

(3)在未来的研究方面,需要对NS在油井固井中的使用进行更多的研究和现场试验,以进一步推动纳米技术在石油天然气工业领域中的应用。与此同时,建议探索不同类型的纳米颗粒协同作用的可能性,由此可能会发现更好的性能和新的应用。

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