

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCIÓN DE NUEVAS CREACIONES**

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Abogado
JUAN PABLO CADENA SARMIENTO

ASUNTO	Radicación	08 118052
	Trámite	002
	Evento	001
	Actuación	519
	Oficio	
	Folios	5

09489

Patente de Invención

☒

Patente de Modelo de Utilidad

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Vía Nacional

☒

Vía PCT (Fase Nacional)

☐

Capítulo I

☐

Capítulo II

☐

No. Solicitud Internacional

Fecha de Presentación Internacional

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Folios 6 a 15	05/Noviembre/2008
Reivindicaciones:	Folios 16 a 17	05/Noviembre/2008
Dibujos:	Folios 19 a 24	05/Noviembre/2008
Prioridad:	US 12/234,920	22/Septiembre/2008

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

Título de la solicitud: "Nano-Aditivo para Operaciones de Cementación de Pozos de Hidrocarburos".

El problema planteado en esta solicitud consiste en la necesidad de proporcionar un nano- aditivo que es particularmente útil en mezclas de cemento, especialmente las mezclas de cemento que van a emplearse para la terminación o demás operaciones de pozos de hidrocarburos.

Expediente 08 118052 1er Art 45

Para resolver este problema técnico la solicitud en estudio proporciona un aditivo de cemento, el cual comprende partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y por lo menos un aditivo seleccionado del grupo conformado por partículas nano-dimensionadas de SiO_2 , $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, Al_2O_3 , P-Ca y combinaciones de los mismos.

El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C 4 B 28/2.

4. De la Solicitud de Patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

Durante la evaluación de claridad y concisión de las reivindicaciones, esta Oficina encontró que:

- Las reivindicaciones 1, 2 y 4, no son claras porque presentan términos generales "*partículas nano-dimensionadas de SiO_2 , $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, Al_2O_3 , P-Ca*", que sugieren de forma imprecisa que la protección se extiende a otras posibles variaciones o modificaciones.
- La reivindicación 6 tiene una falsa dependencia con la reivindicación 1, ya que define "*un producto de cemento, que comprende partículas de cemento y el aditivo de cemento de la reivindicación 1*". Es importante mencionar que las reivindicaciones deben caracterizar un producto por la forma o constitución del mismo, las partes que lo componen y todo lo que permita establecer cómo se llegó a tales resultados
- Las reivindicaciones 7 y 8 no son claras porque presentan resultados a obtener, "*las partículas de cemento forman una matriz cementante que tiene espacios intersticiales y porosidad, y donde el aditivo de cemento ocupa los espacios intersticiales*", "*para proveer una mezcla sustancialmente homogénea de las partículas y las partículas nano-dimensionadas*", "*bajo temperatura controlada y pH para formar un sistema surfactante continuo, que contiene las partículas y las partículas nano-dimensionadas*", lo cual no es permitido, puesto que las citadas reivindicaciones incluirían no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado.

5. Determinación del Estado de la Técnica

El Estado de la Técnica se determinó con base en la fecha de presentación de la solicitud de prioridad: septiembre 22 de 2008 y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Item	Documento	Título	Fecha de Publicación
D1	Artículo 1 ¹	Effects of Nano-Materials on Properties of Waterworks Sludge Ash Cement Paste.	4/Julio/2006
D2	WO 97/49644	Lightweight Thermally Stable Cement Compositions and Method of Use.	31/Diciembre/1997

1 Wen-Ten Kuo, Kae-Long Lin, Wei-Che Chang, Huan-Lin Luo. "Effects of Nano Materials on Properties of Waterworks Sludge Ash Cement Paste" J.IND.ENG.CHEM., vol. 12, no. 5, 2006, divulga (ver resumen, FI.100), la utilización

de partículas nano-SiO₂ en combinación con lodo de ceniza añadido al cemento para reducir la fluidez y acortar el tiempo de fraguado de la pasta de cemento. Además, la pasta de cemento se hace más densa, más uniforme, y se observa resistencia a la compresión después de la adición de nano-SiO₂.

D2<http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=WO&NR=9749644A1&K C=A1&FT=D&ND=4&date=19971231&DB=EPODOC&locale=en> EP divulga (resumen), una composición de cemento ligero térmicamente estable y suspendido, adecuada para el revestimiento de un pozo de sondeo que tiene temperaturas de ajuste en o por debajo de 40 ° C y la temperatura extendida para el uso en exceso de 200 ° C. La composición de cemento tiene una relación de sílice de cal a menos o igual a 1, y la sílice tiene un tamaño medio de partícula menor o igual a aproximadamente 15 micras.

6. Examen de Patentabilidad (Art 14 D486)

Novedad (Art 16 D486)

La reivindicación 1 consiste un aditivo de cemento, que comprende partículas de SiO₂-CaO-Al₂O₃ y por lo menos un aditivo seleccionado del grupo conformado por partículas nano-dimensionadas de SiO₂, 2CaO•SiO₂, 3CaO•SiO₂, Al₂O₃, P-Ca y combinaciones de los mismos.

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1
Aditivo de cemento que comprende:	Lodo que contiene (Fl. 100, Pág. 703, Tabla 1):
Partículas de SiO ₂ -CaO-Al ₂ O ₃	Ceniza SiO ₂ , Al ₂ O ₃ y CaO (Fl. 100, Pág. 703, Tabla 1).
y por lo menos un aditivo seleccionado del grupo conformado por partículas nano-dimensionadas de SiO ₂ , 2CaO•SiO ₂ , 3CaO•SiO ₂ , Al ₂ O ₃ , P-Ca y combinaciones de los mismos.	Un nano-SiO ₂ con un tamaño medio de partícula de 25 nm y cemento Portland (Fl. 100, Pág. 703, Tabla 1).

Las características **esenciales** de la composición del aditivo de cemento de la reivindicación 1 habían sido divulgadas previamente en D1, el cual da a conocer un aditivo de cemento, que comprende partículas de SiO₂-CaO-Al₂O₃ y por lo menos un aditivo seleccionado del grupo conformado por partículas nano-dimensionadas de SiO₂, 2CaO•SiO₂, 3CaO•SiO₂, Al₂O₃, P-Ca y combinaciones de los mismos (Pág. 703, Tabla 1).

En consecuencia, la reivindicación 1 no es nueva ó carece de novedad, según lo divulgado en el documento D1.

Respecto a las reivindicaciones dependientes, el documento D1 determina: la reivindicación 2, donde el aditivo comprende partículas nano-dimensionadas SiO₂, (Pág. 703, Tabla 1); respecto a las reivindicaciones 3 y 5 estas están implícitas. Por tanto, las reivindicaciones dependientes 2 – 5 no mencionan alguna característica que haga nueva a la composición de la reivindicación 1, por lo cual se considera que no son nuevas.

La reivindicación 6 había sido divulgada previamente en D1, el cual da a conocer un producto de cemento, que comprende partículas de cemento y el aditivo de cemento

de la reivindicación 1 (Fl. 100, Pág. 703, Col. 2, líneas 20 – 34 y tabla 1).

La reivindicación 8 consiste en un método para elaborar el aditivo de cemento de la reivindicación 1, que comprende los pasos de:

- Sintetizar separadamente cada una de las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas;
- Mezclar las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas bajo temperatura controlada y pH para formar un sistema surfactante continuo, que contiene las partículas y las partículas nano-dimensionadas; y
- Combinar las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas en un disolvente común para proveer una mezcla sustancialmente homogénea de las partículas y las partículas nano-dimensionadas.

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D2
Método para elaborar el aditivo de cemento, que comprende los pasos de :	Un método de fabricación de cemento con escoria de alto horno para la cementación de pozos (Pág. 4, Mezcla 1).
Sintetizar separadamente cada una de las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas;	La síntesis de las partículas está implícita (Pág. 4, Mezcla 1).
Mezclar las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas bajo temperatura controlada y pH para formar un sistema surfactante continuo, que contiene las partículas y las partículas nano-dimensionadas; y	Se mezclan las partículas de escoria de alto horno y las partículas nano- SiO_2 (Pág. 7, línea 35) y (Pág. 4, Mezcla 1).
Combinar las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas en un disolvente común para proveer una mezcla sustancialmente homogénea de las partículas y las partículas nano-dimensionadas.	Mezclar las partículas nano- SiO_2 (página 7, línea 35) y las partículas de escoria de alto horno en agua (Pág. 4, Mezcla 1).

Las características **esenciales** del método de la reivindicación 8 habían sido divulgadas previamente en D2, el cual conocer un método para elaborar el aditivo de cemento de la reivindicación 1, que comprende los pasos de : sintetizar separadamente cada una de las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas; mezclar las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas bajo temperatura controlada y pH para formar un sistema surfactante continuo, que contiene las partículas y las partículas nano-dimensionadas; y combinar las partículas de $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ y las partículas nano-dimensionadas en un disolvente común para proveer una mezcla sustancialmente homogénea de las partículas y las partículas nano-dimensionadas (Pág. 4, Mezcla 1).

En consecuencia, la reivindicación 8 no es nueva ó carece de novedad, según lo divulgado en el documento D2.

La reivindicación dependiente 9, es un estándar de proceso conocido por una persona versada en la materia que trabaje en la obtención de nano partículas y partículas de tamaño reducido, por tanto, no menciona alguna característica que haga nueva a la composición de la reivindicación 8, por lo cual se considera que no es nueva.

7. Conclusión

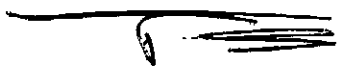
Los requisitos de Patentabilidad de la presente Solicitud están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	Artículo 1	1 - 7	Novedad
D2	WO 97/49644	8	Novedad

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.


JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (C)

El anterior requerimiento fue notificado por fijación en lista, de fecha

05 JUN. 2012
Elaborado por: Yenny Marcela Campos Borda *Yenny Campos Borda*
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Effects of Nano-Materials on Properties of Waterworks Sludge Ash Cement Paste

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Abstract: To extend the beneficial reuse of waterworks sludge, nano-SiO₂ was considered as an additive to improve the engineering properties of waterworks sludge ash cement paste. Waterworks sludge was first incinerated to ash at 800 °C. Different amounts of nano-SiO₂ were added to the sludge ash and then mixed with cement to make a paste. The benefits of using sludge ash as a replacement for cement were assessed. Tests of the fresh paste properties (including flowability and setting time), hardened paste properties (compressive strength), and microstructure analysis (SEM) were performed to assess the influences of the different proportions of nano-SiO₂ and sludge ash added to the paste. Both added admixtures could reduce the flowability and shorten the setting time of the cement paste. Furthermore, the cement paste became denser, more uniform, and exhibited improved early and later compressive strengths after the addition of nano-SiO₂. However, because of the late development of pozzolanic effects, the compressive strengths of the cement paste were reduced with increased amounts of ash replaced. This study indicates that, because Portland cement is well compatible with nano-SiO₂, the performance of silicate cement is improved and the strength of the hardened cement paste is raised, especially for the early strength.

Keywords: cement paste, nano-SiO₂, waterworks sludge ash

Introduction

The rate of tapwater supply has reached 85 % or higher in Taiwan. More than 6000 m³ of waterworks sludge, which needs to be further treated and buried in sanitary landfill locally, is produced each month. It is becoming harder to find land for sanitary landfills in an island like Taiwan. Therefore, applications for resource recovery of waterworks sludge become important. Waterworks sludge contains different kinds of oxides, such as silicon oxide, calcium oxide, iron oxide, and aluminum oxide, as well as rich amounts of clay materials. Retrieving oxides from

sludge and then reusing them in other applications is a direct way to treat sludge waste and can indirectly reduce the demand for natural resources. Lin and coworkers [1] replaced part of clay by waterworks sludge to sinter into cement and found that the strength of cement paste was improved by the waterworks sludge additive. Hence, substituting cementitious materials is a promising application of resource recovery of waterworks sludge.

Cement can provide alkaline catalysts, such as calcium hydroxide, in the pozzolanic reaction. Alkaline catalysts would react with active glassiness ions like aluminum and silicon, to produce silicate hydrates, possibly improving the strength and durability of the cement paste by making the sizes of the pores and particles finer as well as filling up the voids in the paste. With advances of

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Figure 1. SEM image of waterworks sludge ash (5000 x)

Materials and Methods

Materials

(1) Portland Cement: Type I Portland cement produced by a local company in Taiwan was applied. The specific weight was 3.15 and the Blaine specific surface area was 380 m²/kg.

(2) Waterworks Sludge Ash: Waterworks sludge samples were collected from a local waterworks near Kaohsiung City. These samples were oven-dried at 105 °C, incinerated at 800 °C, and then ground to fine particles and passed through a #200 sieve. The chemical components and physical properties of the sludge ash are shown in Table 1 and an SEM image of the sludge ash is shown in Figure 1.

(3) Nano-SiO₂: The chemical components and physical properties of nano-SiO₂ are displayed in Table 1.

Experimental Methods and Parameters

In this study, the water binding ratio [water/cement + waterworks sludge ash] at 0.45 was assigned to the mix. Four different substitution amounts, according to weight percentages of 0, 10, 20, and 30 % of waterworks sludge ash, were proposed and 0, 1, 2, and 3 % of nano-SiO₂ were added as admixtures to each proposed ash substitution in the mix. Note that the total amount of substitution was fixed at 10 %, for example, 9 % of waterworks sludge ash mixed with 1 % of nano-SiO₂. After the proposed materials were mixed well, paste specimens were manufactured at a size of 5.5 × 5 × 5 cm. Flowability and setting time regulated by ASTM C230

Table 1. Chemical Components and Physical Properties of Waterworks Sludge Ash and Nano-SiO₂

Waterworks sludge ash	SiO ₂ (%)	Average particle size (nm)	Specific surface area (m ² /kg)	Specific weight
nano-SiO ₂	99.8	105	200	2.48
Waterworks sludge ash	58.86 % Al ₂ O ₃ : 22.3 % Fe ₂ O ₃ : 6.88 % SO ₃ : 0.39 % MgO: 2.27 % CaO: 4.02 %	25	1720	

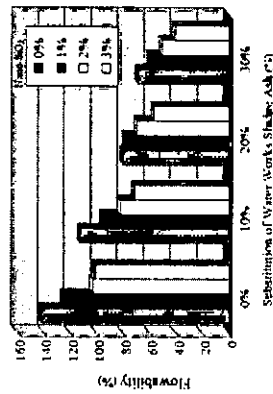


Figure 2. Effects of sludge ash and nano-SiO₂ on the flowability of cement paste.

performed after mixing. Paste specimens were demolded after 24 h after casting and left in a curing room where the humidity and temperature were maintained at 90% and 23 ± 2 °C, respectively. The specimens were then cured in a saturated sodium sulfate solution at 1, 3, 7, 28, and 60 days at a temperature of 23 ± 2 °C. compressive strength tests, as regulated by ASTM C109, were performed at the end of each curing time. To proceed with the study of their microstructural development, parts of the specimens after compressive tests were kept in methanol solution to eliminate the hydration in the paste.

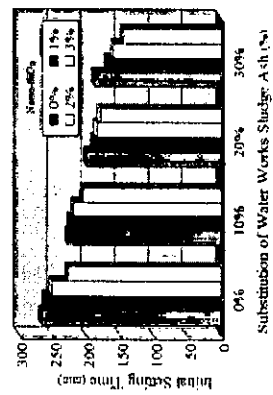


Figure 3. Influence of waterworks sludge ash and nano-SiO₂ on the initial setting time for cement paste

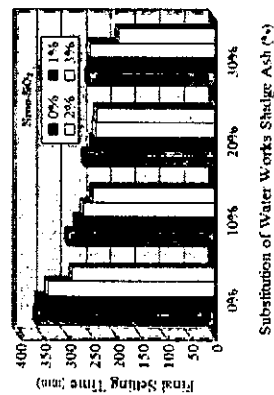


Figure 4. Influence of waterworks sludge ash and nano-SiO₂ on the final setting time for cement waste

were observed for 20 to 30 % additives in the paste. Moreover, when the same portions of binding materials were replaced by both sludge ash and nano-SiO₂, we found that the flowability of the paste decreased with increased quantities of nano-SiO₂ in the mixture.

Influence of Nano-SiO₂ on Setting Time of Sludge Ash
-cement Paste

Results of the initial and final set times of the cement paste with waterworks loading ash and nano-SiO₂ added are shown in Figures 3 and 4, respectively. With the help of the increased fineness of nano-SiO₂, the pastes incorporated with nano-SiO₂ exhibited shorter final set times. This result indicates that nano-SiO₂ has a faster hydration reaction speed than did the cement, because nano-SiO₂ is characterized by its unique surface effects, smaller particle sizes, and higher surface energy [7]. Smaller particle sizes allow a rapid increase in surface area, leading to a quick rise in the rapid increase in surface atoms. These surface atoms are highly active and unstable, which results in a faster reaction speed. Hence, a cautious approach

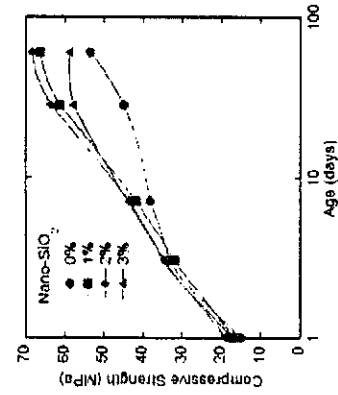


Figure 5. Relationship between compressive strength and curing time for cement paste with nano-SiO₂ added.

should be taken for the setting time of the paste during the application of nano-SiO₂. If necessary, a retarder should be considered as an additive to nano-SiO₂/cement paste. Moreover, the initial and final set times of the pastes were decreased upon increasing the amounts of sludge ash and nano-SiO₂ added. When the same portions of binding materials were replaced by both sludge ash and nano-SiO₂, water absorption of the clear surface effects produced by nano-SiO₂ were noticed that the setting time of the paste decreased with increased amounts of nano-SiO₂-added.

Influence of Nano-SiO₂ on Compressive Strength of Sludge Ash Cement Paste

Figure 5 illustrates the relationships between the curing time and compressive strengths of pastes with different amounts of nano-SiO₂. The addition of nano-SiO₂ at different amounts was very beneficial for the compressive strength of cement paste because more significant at early curing ages. Because of more bonds formed between the surface of Ca(OH)₂ and the surface of C-S-H [calcium silicate hydrate], leading to the production of a C-S-H/calcium silicate hydrate, Ca(OH)₂, and SiO₂-SiO₂-CH₃OH gel, reduction of pores in CH crystals, the compressive strengths of the paste improved [57]. However, an optimum amount of nano-SiO₂ occurred at ca. 2%. When increased the addition of nano-SiO₂ beyond 2%, the compressive strengths of nano-SiO₂ additive was applied.

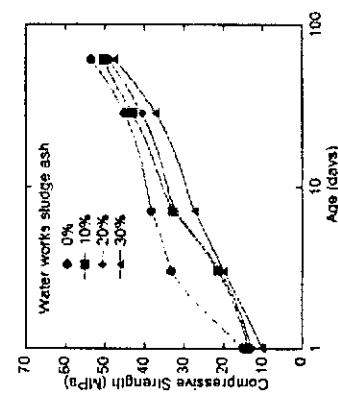


Figure 6. Relationship between compressive strength and

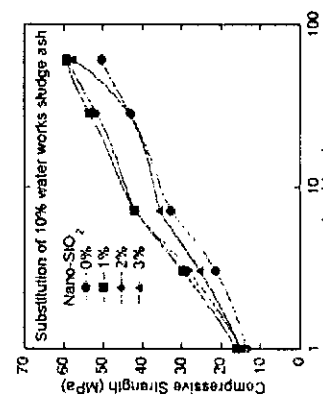


Figure 7. Influence of both 1) °, sludge ash and nano-SiO₂ on the compressive strengths of paste samples.

Why the compressive strength was not as great. This situation is due to the fact that the existence of silicon transformed the original amorphous C-Si-H gel (lower C-Si/H ratio) into $\text{Ca}_2\text{Si}_2\text{H}_6$ (tobermorite) and increase the content of silicate polymerization. When more silicon was added than was necessary for the formation of tober-

Sludge ash Age (days)	10%	20%	30%	40%	50%	10*
1*	1	28	60	1	3	38
2*	119	28	324	132	105	115
3*	199	33	270	111	101	110
4*	133	29	169	101	109	102
5*	113	29	169	101	109	102
6*	113	29	169	101	109	102
7*	113	29	169	101	109	102
8*	113	29	169	101	109	102
9*	113	29	169	101	109	102
10*	113	29	169	101	109	102

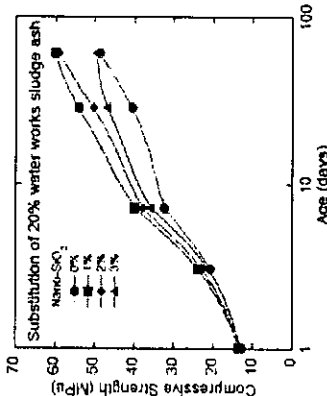


Figure 8. Influence of both 20% sludge ash and nano-SiO₂ on the compressive strengths of paste samples

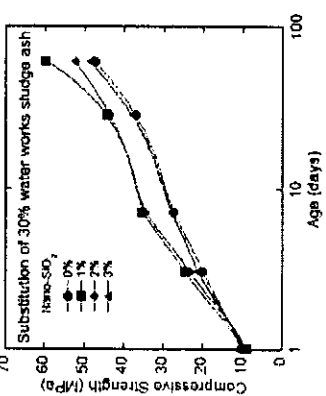


Figure 9. Influence of both 30% sludge ash and nano-SiO₂ on the compressive strengths of paste samples

mortar. Free silien would be produced that could serve only as filler.

Figure 6 displays the relationships between the curing ages and compressive strengths of paste with different amounts of sludge ash added. Because of the non-fully functional pozzolanic effects of waterworks sludge ash, the compressive strength of the paste reduced with the increased addition of sludge ash. However, pozzolanic reactions in sludge ash cement paste were gradually developed with increased curing time. When cured at 60 days, the compressive strengths of the paste for all amounts of sludge ash replaced were 89 to 95 % of those of the control group, which were better than those cured at 3 days (ca. 60 to 78 % times of control group). It indicates that sludge ash served as a filler material and

did not participate in the cementations at early curing ages.

The influences of both sludge ash and nano-SiO₂ on the compressive strengths of paste samples are shown in Figures 7, 8, and 9. These results indicate that nano-SiO₂ could offset the compressive strength reduction caused by the addition of sludge ash. In general, the compressive strengths of the sludge ash cement specimens with nano-SiO₂ added were higher than those without nano-SiO₂ added. Table 2 presents the efficiency of the compressive strength of paste samples, as defined in the equation (1):

$$\text{efficiency of compressive strength} = \frac{CS_{\text{NS/SA}} - CS_{\text{NSA}}}{CS_{\text{NSA}}} \quad (1)$$

where $CS_{\text{NS/SA}}$ is the Compressive Strength of a paste with different amounts of Replacement of Sludge Ash and nano-SiO₂, $CS_{\text{NS/SA}}$ is the Compressive Strength of a paste with different amounts of Replacement of Sludge Ash and nano-SiO₂.

Equation (1) states how efficiently nano-SiO₂ can provide compressive strength for sewage sludge ash cement paste. A larger value of efficiency represents a better improvement for the compressive strength of paste. However, if the value is less than 1.0, the addition of nano-SiO₂ would reduce the compressive strength of the paste. The efficiency was between 1.01 and 1.52 for specimens with 10 and 20 % replacement of sludge ash and 1.0 to 2.0 % of nano-SiO₂ added. When cement paste was prepared with replacement of 30 % sludge ash and cured at 1 day, the efficiency gained from nano-SiO₂ was limited because of the low flowability in sludge ash cement paste that resulted from the addition of nano-SiO₂. However, with the help of the efficiency obtained from nano-SiO₂, the value of the efficiency improved from 1.02 to 1.29 for longer curing ages.

SEM Analysis for Sludge Ash Cement Paste with Nano-SiO₂ Added

Figure 10(a) displays the microstructure of hydrates obtained from the 20 % sludge ash cement paste specimen cured for 1 day. Non-uniform and dense features of the structure are present and no macro-pores are observed. However, many micro-pores are seen in the image, indicating that the interface between the waterworks sludge ash and the C-S-H gel was bonded together well to produce a microstructure with fine and non-uniform particles. Figures 10(b) to 10(d) illustrate microstructures of the hydrates of the cement pastes for both different amounts of waterworks sludge ash and nano-SiO₂ added when cured for 1 day. No clear pozzolanic reaction was evident for the sludge ash cement paste in Figure 10(a). However, nano-SiO₂ can induce hydration reactions to

Table 3. Analysis of Pore Structures of Cement Pastes with Waterworks Sludge Ash and Nano-SiO₂ Added (Based on Power's Classifications)

Waterworks sludge ash (%)	Nano SiO ₂ content (%)	Age (days)	Capillary pore volume (cm ³ /g)	Gel pore volume (cm ³ /g)	Total pore volume (cm ³ /g)
0	0		0.0511	0.0693	0.11131
0	1		0.0392	0.0914	0.1306
0	2		0.0466	0.121	0.1676
0	3		0.0378	0.1251	0.1629
10	0	3	0.0688	0.127	0.1815
10	1		0.0418	0.1208	0.1626
10	2		0.0353	0.1196	0.1549
10	3		0.0273	0.1014	0.1287
20	0		0.0378	0.0183	0.0561
20	1		0.0159	0.0453	0.0612
20	2		0.0187	0.0601	0.0788
20	3		0.0144	0.0657	0.0801
30	0	28	0.0144	0.0282	0.0426
30	1		0.0146	0.0528	0.0671
30	2		0.0101	0.0338	0.0439
30	3		0.0072	0.0369	0.0441

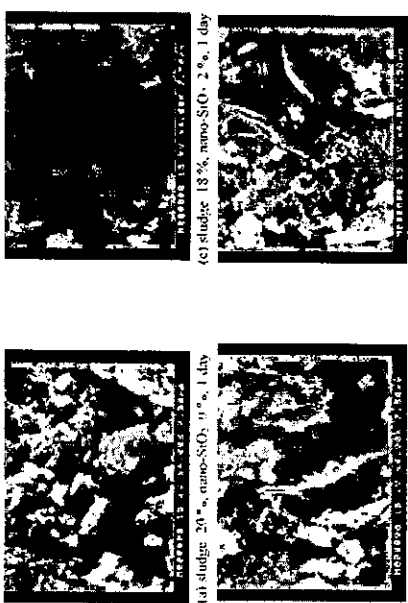


Figure 10. Microstructure of hydrates of cement pastes for both different amounts of waterworks sludge ash and nano-SiO₂ added when cured at 1 day

produce fibrous and networked C-S-H on the CH surface layer, as shown in the Figure 10(b) for the paste with 1 % nano-SiO₂ added. Furthermore, Figure 10(c), for the paste with 2 % nano-SiO₂ added, shows that the CH surface layer was also covered by a layer of C-S-H. The needle-like ettringite was visible inside the pores. Hence, with the addition of nano-SiO₂, the hydrates became denser, finer, and more uniform. Framework structures were

formed by the crosslinked network. The denseness of the paste was increased by filling up the spaces among the framework structure with denser hydrates. As a result, the addition of nano-SiO₂ could reinforce the compressive strength of the paste specimens by improving the micro-structure of the interface to form a denser and more uniform state.

Analysis of Pore Structure

Capillary pores and gel pores are commonly seen in cement paste. Gel pores (pore sizes less than 10 nm), which are part of hydrates, affect the shrinkage and creep of cement paste, but have little influence on permeability. Capillary pores (pore sizes larger than 10 nm), formed from water spaces unoccupied by solid hydrates after the cement paste hardens, are the main impacts on the strength and permeability of the paste. Furthermore, pore structures of hardened cement paste are characterized by the total pore volume and pore connectivity, as well as the size and volume distribution of the pores. In general, due to the progression in the degree of hydration, the effects of a high specific surface area from nano-SiO₂ and turning CII into later hydrates, which mainly contained C-S-H gel and C-A-H (calcium aluminic hydrate) in the late pozzolanic reaction of waterworks sludge ash, the pore sizes gradually changed from large into small pores for the cement paste with sludge ash and nano-SiO₂ added. Table 3 shows the results obtained from mercury intrusion porosimetry (MIP) measurements with the pressure set at 60,000 psi. Note that the total amount of additive is fixed at 10 % for example, 9 % of waterworks sludge ash mixed with 1 % of nano-SiO₂. When cured at 3 days, due to either the waterworks sludge ash or nano-SiO₂ not fully participating in the initial reaction and being insufficient for filling up the spaces left in the early hydration, the total pore volumes observed in the specimens with sludge ash or nano-SiO₂ added were greater than those in the control group. The strength of the paste reduced with the increase in the amount of sludge ash added. Although the total pore volumes increased in the amount of from 11.31 to 16.76 % with the increase in the amount of nano-SiO₂, the increase was mainly reflected in smaller pore sizes (<10 nm) from 5.9 to 12.51 %. In contrast, pore sizes larger than 10 nm were reduced from 5.41 to 3.78 %. This result indicates that nano-SiO₂ (with a higher specific surface area) was the main component that reacted quickly with CII in the early hydration. However, when cured at 28 days and with the help of pozzolanic reactions [8-10], suitable amounts of waterworks sludge ash added could consume CII (larger crystallizations) to form C-S-H and C-A-H (smaller crystallizations), which would make the structure of the crystalline phase denser. Therefore, the pore volumes reduced, the sizes of the pores become smaller, and the strengths of the paste in the test groups were better than those in the control group. As part of the sludge ash was replaced by nano-SiO₂, the effects of the higher specific surface area of nano-SiO₂ became evident and resulted in the reduction of the total pore volumes and the growth in the strengths of the paste specimens. Table 3 also shows that, with the proposed different substitutions of additives and the increasing curing ages, the total pores volume of cement

paste gradually decreased and the pores size distribution turned from capillary pores into gel pores. This situation indicates that hydrates, such as C-S-H gel, in the paste grew gradually to make the structure of the crystalline phase denser and more uniform, while waterworks sludge ash led to erosion by CII. Moreover, after the addition of different proportion of nano-SiO₂, radiate-like C-S-H fibers produced by the hydration of different particle sizes weaved alternately to form denser network structures. Furthermore, large pores originally filled with water were replaced by these hydrates, which made the sizes of the pores smaller. As the pore volumes reduced, the strength of the cement paste increased with the increase of the curing time. Furthermore, when part of the sludge ash was replaced by nano-SiO₂, the total pore volumes reduced and the strength of the paste increased in the test groups because they took advantage of the high specific surface areas of nano-SiO₂.

Conclusions

In this study, results were obtained by directly comparing different amounts of replacement of waterworks sludge ash in cement paste and various quantities of nano-SiO₂ added to the paste on the basis of experimental data. Results are summarized as follows:

- 1) The flowability and workability of paste specimens reduced with the increase of waterworks sludge ash and nano-SiO₂ added. However, consistency increased with both admixtures.
- 2) The initial and final set times of the cement paste specimens became shorter with the increase of waterworks sludge ash and nano-SiO₂ added.
- 3) The compressive strength of the cement paste increased with the quantity of nano-SiO₂ added to the specimens. In this study, our results indicate that the optimum amount of nano-SiO₂ added is ca. 2 %. The compressive strength of cement paste reduces with the increase in the amount of waterworks sludge ash added. However, due to the effects of pozzolanic reactions, the compressive strengths of the sludge ash cement paste at later curing times were close to those obtained in the control group. Our results indicate that nano-SiO₂ could offset the compressive strength reduction caused by the addition of the sludge ash.
- 4) With the application of nano-SiO₂ to paste specimens, framework structures were formed by cross-linked networks in the cement-based materials. The denseness of the paste increased by filling up the spaces among the framework structure with denser hydrates. Hence, the nano-SiO₂ additive could reinforce the early and later compressive strength developments of the paste specimens by improving the microstructure of the interface to provide a denser and more uniform state.

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