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RESEARCH ARTICLE

RESEARCH OF THE SYNTHESIS OF CEMENT GRINDING INTENSIFIERS FROM GAS PROCESSING WASTE AND SECONDARY RAW MATERIALS

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Abstract. *This article presents the results of a study exploring the potential use of gas processing waste as a raw material for synthesizing cement grinding intensifiers. Effective raw materials for synthesizing grinding intensifiers were identified: methyldiethanolamine (a gas processing waste) and hydrolyzed polyacrylonitrile (HIPAN) obtained from recycled nitrofiber. The use of alkanolamines as a raw material for synthesizing grinding intensifiers was substantiated. Physicochemical methods demonstrated the effectiveness of the methyldiethanolamine purification method. Optimal conditions for synthesizing grinding intensifiers were determined. Physicochemical analysis of the resulting grinding intensifiers revealed that all compositions exhibit a very strong C=O (amide) peak at 3300 cm^{-1}, a broad N-H elongation peak at 1236 cm^{-1}, and a strong C-N (amide III) elongation, which together confirm the clear presence of the amide group (-CONH-) required for grinding intensifiers. It was determined that the cumulative distribution curve of the product obtained with the addition of 0.25% of the synthesized grinding intensifiers G+M and G+T shifts toward finer grinding due to the unique combination of active components (alkanolamines, HIPAN), which allows them to act synergistically. HIPAN provides increased efficiency due to its high basicity, which reduces the electrostatic attraction between particles, leading to finer grinding and increased productivity.*

Keywords: *cement grinding intensifiers, alkanolamines, energy efficiency, production waste.*

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ҒЫЛЫМИ МАҚАЛА

ГАЗ ӨҢДЕУ ҚАЛДЫҚТАРЫ МЕН ЕКІНШІ РЕТТІК ШИКІЗАТТАН АЛЫНҒАН ЦЕМЕНТТІ ҰНТАҚТАУ ЖЕДЕЛДЕТКІШТЕРІ СИНТЕЗІН ЗЕРТТЕУ

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Аңдатпа. *Бұл мақалада цементті ұнтақтау жеделдеткіштерін синтездеу үшін шикізат ретінде газ өңдеу қалдықтарын пайдалану мүмкіндігін зерттеу нәтижелері келтірілген. Ұнтақтауға арналған қоспаларды синтездеу үшін тиімді шикізат материалдары анықталды: метилдиэтаноламин-газ өңдеу қалдықтары және екінші реттік нитрофибра негізінде алынған гидролизденген полиакрилонитрил (ГИПАН), ұнтақтау жеделдеткіштерін синтездеу кезінде алканоламиндерді шикізат ретінде қолдануға негізделген. Физика-химиялық әдістермен метилдиэтаноламинді тазарту әдісінің тиімділігі анықталды. Жеделдеткіштер синтезінің оңтайлы шарттары анықталды. Алынған жеделдеткіштерді физика-химиялық талдау нәтижелері бойынша барлық құрамдарда C=O (амид) 3300 см⁻1 өте күшті шыңы, N-H ұзарудың кең шыңы, 1236 см⁻1 және C-N (амид III) күшті кеңеюі көрінетіні анықталды, бұл қажетті ұнтақтағыш қоспалармен бірге амид тобының (-CONH-) айқын болуын растайды. Г+М және Г+Т ұнтақтау үшін 0,25% синтезделген қоспаларды қосу арқылы алынған өнімнің жиынтық таралу қисығы белсенді компоненттердің (алканоламиндер, ГИПАН) бірегей жиынтығының арқасында аса ұсақ ұнтақталу жағына ауысады және оларға синергетикалық әрекеттесуге мүмкіндік береді. ГИПАН жоғары негізділігінің арқасында тиімділікті арттыруды қамтамасыз етеді, бұл бөлшектер арасындағы электростатикалық тартылуды азайтады, нәтижесінде аса ұсақ ұнтақтауға әкеледі және өнімділікті арттырады.*

Түйін сөздер: *цементті ұнтақтау жеделдеткіштері, алконаламиндер, энергия тиімділігі, өндіріс қалдықтары.*

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НАУЧНАЯ СТАТЬЯ

ИССЛЕДОВАНИЯ СИНТЕЗА ИНТЕНСИФИКАТОРОВ ПОМОЛА ЦЕМЕНТА ИЗ ОТХОДОВ ГАЗОПЕРЕРАБОТКИ И ВТОРИЧНОГО СЫРЬЯ

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Аннотация. *В данной статье приведены результаты исследования возможности использования отходов газопереработки в качестве сырья для синтеза интенсификаторов помола цемента. Определены эффективные сырьевые материалы для синтеза добавок для измельчения: метилдиэтаноламин - отходы газопереработки, и гидролизованный полиакрилонитрил (ГИПАН), полученный на основе вторичного нитроволокна, обоснована применение алканоламинов в качестве сырья при синтезе интенсификаторов помола. Физико-химическими методами установлены эффективность метода очистки метилдиэтаноламина. Определены оптимальные условия синтеза интенсификаторов. Результатами физико-химического анализа полученных интенсификаторов установлено, что во всех составах проявляется очень сильный пик C=O (амид) 3300 см$^{-1}$, широкий пик удлинения N-H, 1236 см$^{-1}$ и сильное удлинение C-N (амид III), которое вместе подтверждают явное присутствие амидной группы (-CONH-) необходимых для добавок измельчителей. Определено, что совокупная кривая распределения продукта, полученного с добавлением 0,25% синтезированных добавок для измельчения Г+М и Г+Т, смещается в сторону наиболее мелкого помола благодаря уникальному сочетанию активных компонентов (алканоламины, ГИПАН), которые позволяют им действовать синергетический. ГИПАН обеспечивает повышенную эффективность благодаря своей высокой основности, которая снижает электростатическое притяжение между частицами, что приводит к более тонкому помолу и повышению производительности.*

Ключевые слова: *интенсификаторы помола цемента, алканоламины, энергоэффективность, отходы производства.*

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CONFLICT OF INTEREST

The authors state that there is no conflict of interest.

The authors declare that no generative artificial intelligence technologies or AI-based tools were used in the preparation of this article.

АЛҒЫС/ҚАРЖЫЛАНДЫРУ КӨЗІ

Зерттеу Қазақстан Республикасы Ғылым және жоғары білім министрлігі Ғылым комитетінің AP26102705 «Жергілікті шикізаттар негізінде цементті ұнтақтау жеделдеткіштерін әзірлеу және алу» ғылыми жобасы шеңберіндегі гранттық қаржыландыруы аясында жүргізілді.

МҮДДЕЛЕР ҚАҚТЫҒЫСЫ

Авторлар мүдделер қақтығысы жоқ деп мәлімдейді.

Авторлар мақаланы дайындау барысында генеративті жасанды интеллект технологиялары мен жасанды интеллектке негізделген технологияларды пайдаланбағанын мәлімдейді.

БЛАГОДАРНОСТИ/ИСТОЧНИК ФИНАНСИРОВАНИЯ

Исследование выполнено в рамках грантового финансирования Комитета науки Министерства науки и высшего образования Республики Казахстан (проект AP26102705 «Разработка и получение интенсификаторов помола цемента на основе местного сырья»).

КОНФЛИКТ ИНТЕРЕСОВ

Авторы заявляют, что конфликта интересов нет.

Авторы заявляют о том, что при подготовке статьи не использовались технологии генеративного искусственного интеллекта и технологии, основанные на искусственном интеллекте.

1 INTRODUCTION

Grinding is one of the most labor-intensive and energy-intensive processes in cement production. Approximately 85% of the electricity consumed in cement production is used to grind raw materials and grinding materials, including 50% to grind cement clinker. Therefore, intensifying grinding equipment and upgrading grinders leads to improved product quality and energy and fuel savings. Cement quality depends primarily on the quality of its grinding. The fineness of cement grinding increases the total surface area of its particles, enhances hydration activity, and increases the strength of the cement stone (especially during the initial hardening period). However, increasing the fineness inevitably leads to particle aggregation and reduced grinding efficiency due to increased surface energy **(Ovcharenko, 1990; Rebinder, 1972; Cahn et al., 1964)**. Therefore, intensifying fine grinding processes, i.e., increasing their efficiency, is a pressing issue. The use of chemical additives is considered a low-cost and highly effective method for intensifying the performance of grinding equipment.

In this regard, the aim of this study is to develop and scientifically substantiate the synthesis of additives-intensifiers for cement clinker grinding based on gas processing waste, ensuring an increase in grinding fineness and a reduction in energy costs while maintaining or improving the properties of cement.

Research showed that during cement grinding, the specific surface area of the particles increases to a certain point, after which, due to the agglomeration of fine cement particles and their adhesion to the surface of the balls and mill lining, the dispersion begins to decrease **(Yang et al., 2019; Huang et al., 2016; Li et al., 2020; Riding et al., 2010; Moldamuratov et al., 2023)**. Currently, ball mills still account for 60% of all mills used in cement production **(Yang et al., 2019)** and reducing the energy consumption of the grinding process remains highly relevant. Factors that can reduce energy consumption by changing the specified design and technological characteristics of grinding equipment include the use of various chemical additives.

The task of developing a classification of chemical additives was driven by the need to identify and substantiate the features characterizing groups of chemical additives in cement grinding, in order to shape, predict, and regulate their properties, as well as to develop new highly effective cement compositions.

According to the classification of chemical compounds, most organic compounds recommended as grinding intensifiers are amines and glycols **(Gholizadeh Vayghan et al., 2021)**.

Various alkanolamines are widely used in the production of cement grinding intensifiers. Furthermore, alkanolamines are widely used in the processing of natural and associated gas, which ranks Kazakhstan among the world's leading countries in hydrocarbon reserves, production, and processing **(Suleimenov et al., 2022)**. According to statistics, proven natural gas reserves in Kazakhstan amount to 3.8 trillion cubic meters, of which 2.2 trillion cubic meters are associated petroleum gas and 1.6 trillion cubic meters are natural gas **(Yang et al., 2019)**. In the first six months of 2025, natural and associated gas production in the republic increased by 18.3%, reaching 5.73 billion cubic meters **(Yang et al., 2019)**.

Since natural and associated petroleum gas produced by oil and gas companies contains a number of corrosive components, such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2), transporting these gases without prior purification to remove H_2S and CO_2 leads to corrosion of gas pipelines and installations, environmental pollution, and a decrease in gas quality.

Flaring associated petroleum gas is harmful to the environment because it produces sulfur dioxide, making this process hazardous. In the atmosphere, sulfur dioxide reacts with atmospheric oxygen to form sulfur dioxide (SO_3), which turns into sulfuric acid aerosol, which falls to the ground with precipitation. Such acid rain leads to the acidification of soil and natural waters, and, consequently, to the development of acid corrosion of various building structures **(Nabokov et al., 2015)**.

In Kazakhstan, there are currently several oil refineries that process associated petroleum gases, and these enterprises use aqueous solutions of absorbents such as diethanolamine (DEA),

methyldiethanolamine (MDEA) when processing natural and associated gas, but due to the fact that methyldiethanolamine is resistant to thermal and chemical decomposition, and also practically does not mix with hydrocarbons, many enterprises use MDEA **(Scrivener et al., 2018; Nabokov et al., 2015)**.

The average MDEA consumption for purifying one cubic meter of gas flow depends on the gas composition, concentration of harmful substances, and specific purification technologies. Typically, approximately 0.1 to 0.5 kg of MDEA is consumed for neutral and moderately polluted gases. There are no specific published data on the volume of saturated MDEA waste in Kazakhstan. However, given the extensive use of this chemical in the oil and chemical industries for the production of anti-corrosion compounds and other products, it can be assumed that its waste is generated in significant quantities. Interestingly, MDEA is a substance with absorbent and cleaning properties, and its waste requires strict environmental control due to potential toxicity and the difficulty of disposal.

Alkanolamines are organic compounds containing both hydroxyl (-OH) and amino groups (-NH_2, -NHR, and -NR_2). There are several types of alkanolamines, including triethanolamine (TEA), triisopropanolamine (TIPA), ethanolisopropanolamine (DEIPA), and ethyldiisopropylamine (EDIPA) **(Juenger et al., 2019; Snellings et al., 2016; Kabdushev et al., 2023)**. The intermolecular polarization of alkanolamine compounds is directly proportional to their molecular weight. For triethanolamine (TEA) and triisopropanolamine (TIPA), these values are maximum and amount to 15.13 and 20.59, respectively, therefore, these compounds provide the highest possible grinding effect. When used as grinding intensifiers, they prevent the agglomeration of cement particles, which leads to a finer particle size distribution and reduced energy consumption in the grinding process. The grinding efficiency varies depending on the dosage of alkanolamines **(Pan et al., 2019; Gholizadeh Vayghan et al., 2021; Lothenbach et al., 2019)**. Therefore, the introduction of an appropriate amount of grinding intensifier in the grinding process is of practical importance.

The process of modifying alkanolamines is usually carried out using esterification methods, esterification is generally defined as the reaction between a carboxylic acid and an alcohol in the presence of a catalyst to form an ester **(Welch, 1947)**. Esterification was carried out to replace the hydroxyl groups of the TEA molecule with a carboxyl group of higher polarity. For this purpose, two different monocarboxylic acid compounds were esterified with TEA to form a modified TEA ester. Monocarboxylic acids with short hydrocarbon chain length (1-3 atoms) and medium chain length (4-8 carbon atoms) were selected. A catalyst compatible with the reaction structure of the selected carboxylic acids and alkanolamines was identified through preliminary experiments **(Zhou et al., 2024; Assaad, 2017)**.

Foreign researchers found that the use of alkanolamines as grinding intensifiers reduces the time required to achieve a specific surface area of 4500 (±50) cm^2/g, thereby increasing grinding efficiency. DEA provides the greatest improvement, approximately 8%. These improvement ranges are similar to those observed for alkanolamines or alkanolamine-containing grinding intensifiers in the literature for clinker and cement experiments **(Assaad, 2017)**, although higher values were also reported experiments **(Katsioti et al., 2009; Zhou et al., 2024)**. Since dosing was performed by weight, the number of molecules available to cover the particle surface will vary depending on the type of grinding agent. A plot of grinding efficiency versus the number of moles per unit surface area shows a clear correlation. Therefore, the main reason for the differences in efficiency appears to be related to changes in particle coating caused by changes in molecular weight, while the chemical composition and molecular structure of the alkanolamine itself appear to have a limited influence. This is in contrast to the results obtained for cement and clinker, where, for example, TIPA often provides similar or better grinding efficiency than TEA, despite a lower dosage at the molecular level experiments, since it is somewhat more effective in reducing agglomeration energy experiments **(Hallet et al., 2025; Pontikes, 2025)**.

The authors experiments (found that the addition of alkanolamines to the mixing water leads to the formation of additional monosulfate aluminate (MSA) and C-S-H in the order DEA, DIPA < TEA < TIPA, which is similar to the order of the initial dissolution rates and cumulative heat of reaction R_3. The effect is less pronounced when using alkanolamines as grinding intensifiers, since the amount

of alkanolamine is approximately halved, as discussed previously. Tertiary alkanolamines remain more effective in stimulating the formation of MSA and C-S-H, although there is no clear difference between TEA and TIPA, unlike the addition of alkanolamine alone to the mixing water.

The analysis shows that akanolamines are effective raw materials for the synthesis of grinding intensifiers; however, the compatibility of the resulting cement product with various additives was not fully studied.

From the above it follows that alkanolamines and gas processing wastes, when further purified, can serve as effective raw materials, and the development of cement grinding intensifier additives based on them is a pressing task, the solution to which is to increase the energy efficiency of cement production without reducing its physical and mechanical properties and allowing for the disposal of production waste.

2 MATERIALS AND METHODS

Polyacrylonitrile and various alkanolamines were used as raw materials for the synthesis of cement grinding intensifiers.

To purify secondary alkanolamines, they were first filtered and passed through a fixed bed of activated carbon. The filtered and activated carbon-passed alkanolamines were then purified using a cation exchanger and anion exchanger. To do this, the KU 2-8 cation exchanger was first placed in a 3% hydrochloric acid solution for 24 hours, and the AN-31 anion exchanger was placed in a 5% alkali solution for 24 hours. After 24 hours, the alkanolamines, passed through activated carbon, were then alternately passed through the cation exchanger and anion exchanger.

HIPAN synthesis (hydrolysis of polyacrylonitrile) was carried out in a 500 ml round-bottomed flask equipped with a reflux condenser. 220 ml (0.44 mol) of 8% sodium hydroxide solution was added, followed by 20 g (0.5 mol) of finely ground polyacrylonitrile. The mixture was heated in an oil bath to boiling (bath temperature approximately 100-110°C) and held for approximately 13 hours. When the solution became colorless and transparent, heating was stopped, the solution was cooled, and poured into a 500 ml beaker. The solution was neutralized with 0.5 N hydrochloric acid to a pH of 8-8.2 using a universal indicator.

Sodium polyacrylate was precipitated from the solution by adding 150 ml of methanol. The purified sodium polyacrylate was air-dried for 48 hours.

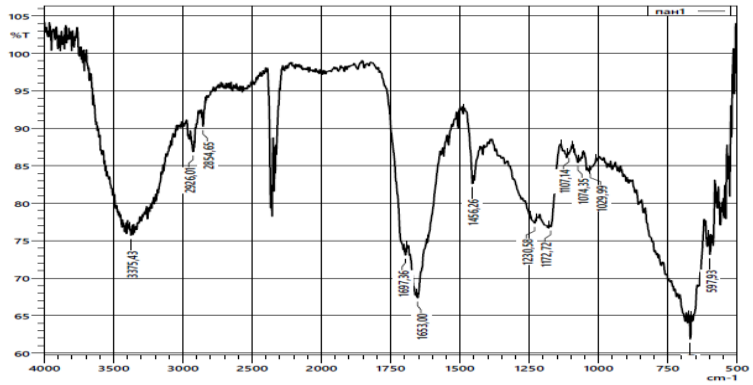

Figure 1 – IR spectra of HIPAN (authors' materials)

Physicochemical analysis revealed that the HIPAN spectrum contains two strong carbonyl peaks at 1697 cm¹ and 1653 cm¹. This indicates the presence of a carboxylic acid (1697 cm^{-1}) and an amide (1653 cm^{-1}) group simultaneously, indicating a compound containing both acid and amide groups in a single molecule.

The broad peak at 3375 cm¹ typically corresponds to O-H (specific for carboxylic acids) or N-H bonds. If it is N-H, this further confirms the presence of an amide group.

The peaks at 2926 and 2854 cm¹ indicate an abundance of methylene (CH_2) groups, while the peak at 1456 cm¹ indicates their bending vibrations. This indicates the presence of a long carbon chain or an aliphatic component.

Strong peaks in the range of 1697 cm^{-1} (C=O) and 1230-1172 cm^{-1} (C-O) are a clear indication of the carboxylic acid group.

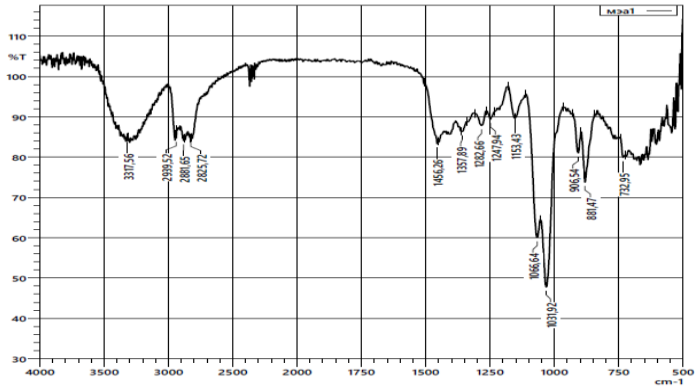

Figure 2 – IR spectra of monoethanolamine (MEA) (authors' materials)

The IR spectrum of purified monoethanolamine shows a strong C=O peak at 1697 cm^{-1}. There are no carbonyl peaks near 1700 cm^{-1} in this spectrum. This means that the sample does not contain carboxylic acid, amide, ketone, or aldehyde groups. The absorption lines at 2825 cm^{-1} are characteristic of the C-H extension of the methoxy group (O-CH_3). This is a very important metric. Strong C-O absorption lines at 1282, 1247, and 1153 cm^{-1} indicate the presence of an ether bond (C-O-C). The broad absorption lines at 3377 cm^{-1} are due to the O-H bond, but this is not a carboxylic acid, but an O-H bond of the alcohol type.

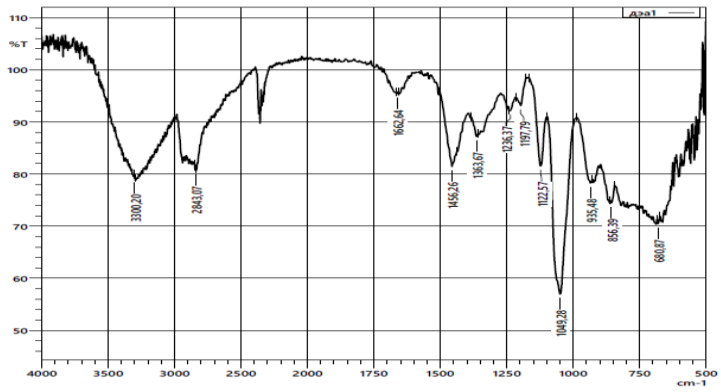

Figure 3 – IR spectra of diethanolamine (DEA) (authors' materials)

The IR spectrum of diethanolamine shows a very strong C=O (amide) peak at 3300 cm^{-1}, a broad N-H extension peak at 1236 cm^{-1}, and a strong C-N extension (amide III). These three peaks together confirm the clear presence of an amide group (-CONH-).

The carbonyl peak is located at 1662 cm^{-1}, which is generally characteristic of amides. However, the presence of N-H peaks suggests this is the case. 2843 cm^{-1} and 1456 cm^{-1} are CH_2 groups (has a carbon chain). 1122 and 1049 cm^{-1} are C-O (contains an alcohol or ether group).

PetroKazakhstan Oil Products LLC primarily uses methyldiethanolamines (MDEA) as adsorbents for gas purification.

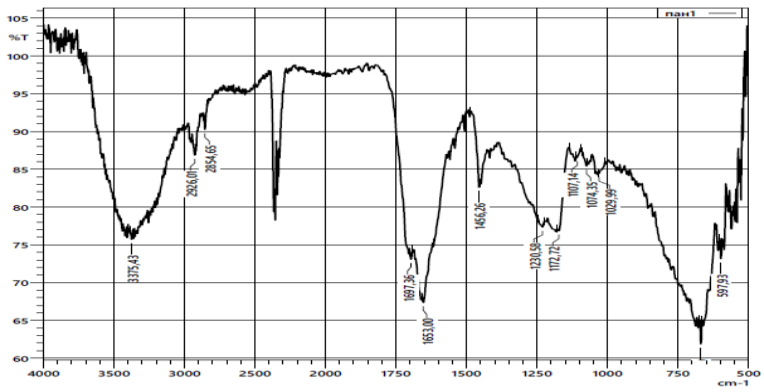

Figure 4 – IR spectra of methyldiethanolamine (MDEA) (authors' materials)

In the IR spectrum of purified MDEA, the C=O peak is absent, the ν(OH) peak is broad at 3600-3000 cm^{-1}, 2970-2870 cm^{-1} C-H; is strong at 1260-1000 cm^{-1} C-O/C-N. The ν(OH) absorption bands become broader and decrease further downwards (protonation + H-bond network increases).

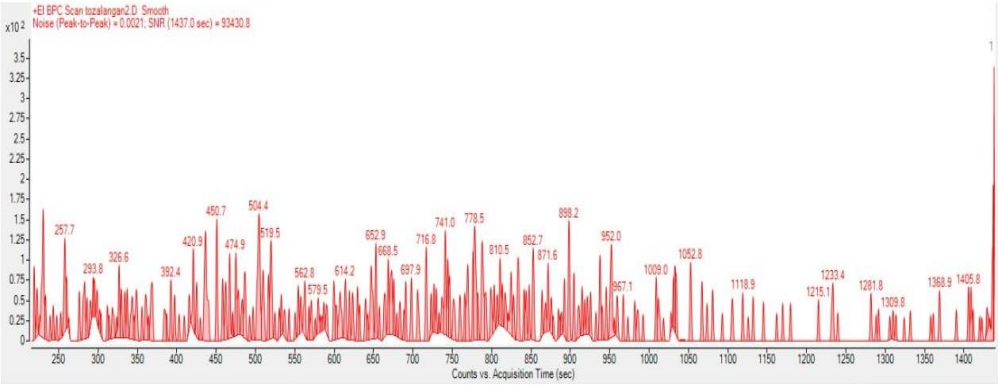

Figure 5 – Chromatographic and mass spectrometric analyses of MDEA (authors' materials)

Mass spectroscopic analysis of purified methyldiethanolamine revealed SNIR = 9340.8 (very high), Noise = 0.0021 (very low), and minimal impurities. Peaks lost during purification: loss of many small peaks present in the litter, significant reduction of contamination peaks in the 300-500 m/z range.

Purification was effective, but the peak at 283.8 m/z is still present. High molecular weight compounds (892-1400 m/z) are completely lost. The signal-to-noise ratio is very high, indicating the sample is well purified. Purified MDEA is easy to use.

No carbonyl (C=O) bands are observed in the IR spectrum of TEA, indicating low oxidized/esterified contamination. Very broad ν(OH) lines at 3600-3000 cm^{-1} indicate TEA's multipoint H-bonding capacity and (often) moisture entrapment. Aliphatic C-H lines at 2970-2870 cm^{-1} and -CH_2 strains in the 1465-1300 cm^{-1} range should appear consistent as a "background". Strong, broad C-O/C-N columns in the 1150-1050 cm^{-1} range are the primary TEA "fingerprint", the most sensitive zone for monitoring the amount of TEA in mixtures. If the signal is absent at 1635-1645 cm^{-1} or if it is too weak, moisture is low.

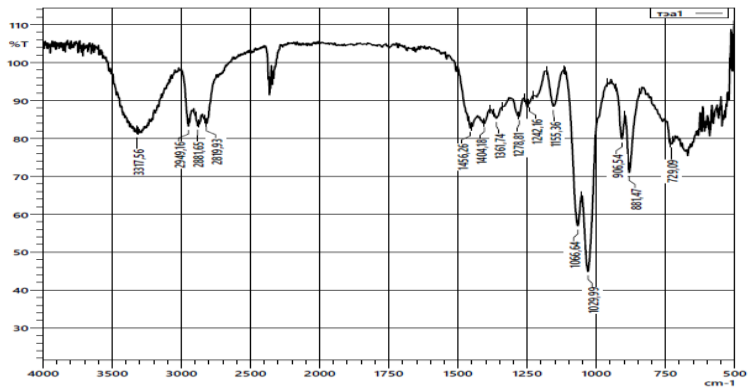

Figure 6 – IR spectra of triethanolamine (TEA) (authors' materials)

The synthesis of a grinding intensifier based on hydrolyzed polyacrylonitrile and various alkanolamines was carried out in a 5-liter reactor, into which the calculated amount of hydrolyzed polyacrylonitrile was placed. The reactor temperature was raised to 50°C, and the calculated amount of alkanolamines was slowly added over 1 hour. The reaction mixture was then cooled to room temperature. Unreacted alkanolamines were separated from the cooled reaction mixture by vacuum distillation. The resulting product is a viscous liquid whose color can vary from light yellow to orange.

Experimental studies showed that the optimal reaction conditions for polyacrylic acid obtained from hydrolyzed polyacrylonitrile with alkanolamine groups are: a temperature of 40-45°C, a reaction time of 6 hours, and an initial loading ratio of 1:9. The fact that virtually identical optimal conditions were obtained for all aminoalkanols is explained by the similarity of their chemical properties. The selection of the starting materials in a 1:9 ratio is also important, as excess alkanolamines also serve to enhance the efficiency of grinding intensifiers.

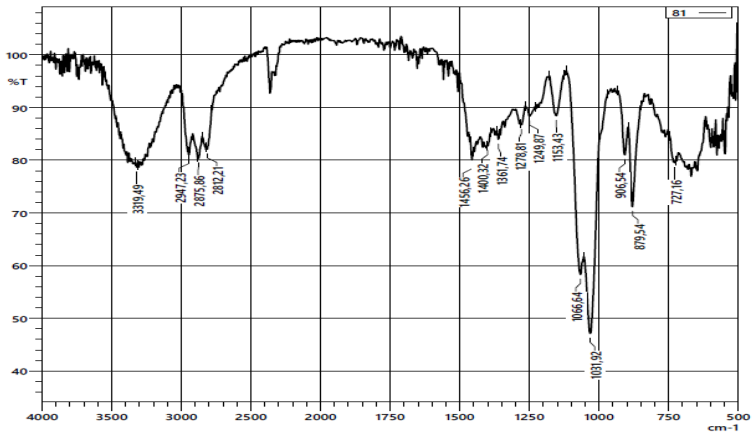

Figure 7 – IR spectra of HIPAN + MEA at a ratio of 1:9 (authors' materials)

The methoxy group (-OCH_3) is clearly visible in both spectra, indicating chemical similarities between the two samples. In the HIPAN + MEA spectrum, a broad peak at 3319 cm^1 and new strong peaks at 1066 and 1031 cm^1 indicate the addition of a primary alcohol (-CH_2-OH) and possibly amine/amide groups.

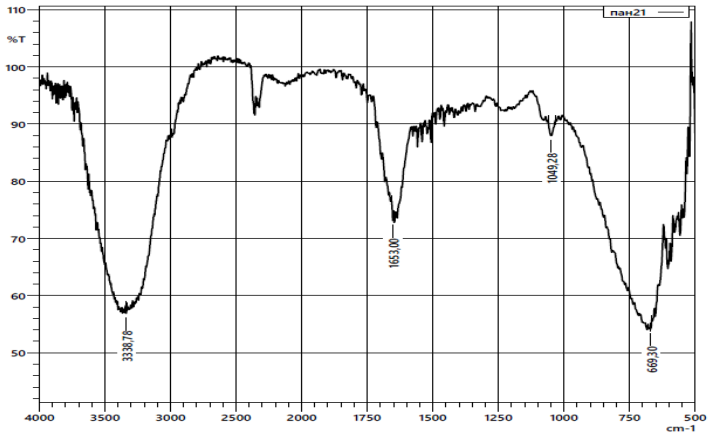

Figure 8 – IR spectra of HIPAN and diethanolamine(authors' materials)

In the IR spectrum of HIPAN+DEA, a reduction or loss of the C≡N peak is observed, indicating the conversion of nitrile groups to amides or carboxyl groups as a result of hydrolysis. A peak near 1730 cm^{-1} indicates the presence of carbonyl (C=O), which is characteristic of hydrolyzed or modified PAN. Broad absorption in the range of 3400-3500 cm^{-1}(if present in the spectrum) represents ν(O-H) or ν(N-H) vibrations, indicating increased hydrophilic properties. New vibrations in the range of 1200-1000 cm^{1} indicate the formation of ester or amine groups in the polymer structure.

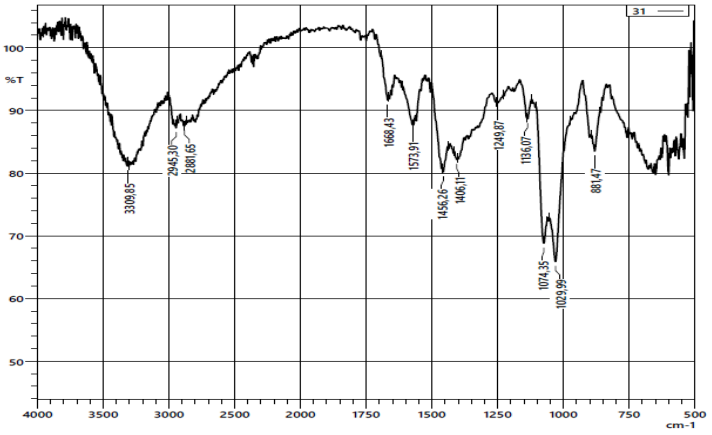

Figure 9 – IR spectra of HIPAN + methyldiethanolamine (at a ratio of 1:9, HIPAN + MDEA)(authors' materials)

Analysis showed that neutralization is insignificant: the -COOH peak is preserved at 1715-1730 cm^{-1}(sometimes sharply observed around 1735 cm^{-1}). $-COO^-$ has a pair of peaks, but they are relatively slow; Δν is smaller (the proportion of ion pairs is smaller). The absorption bands at 3600-3000 cm^- are higher (less H-bonding), because they contain fewer carboxylammonium salts due to the low MDEA. The -C≡N line at ~2240 $cm^{-1}$is relatively precise – the level of hydrolysis may seem somewhat lower. MDEA does not form an amide directly, because it is a tertiary amine, but it deprotonates -COOH as a $-COO^-$ backbone ... H^+MDEA forms an ion pair. This is confirmed by the decrease in ν(C=O)(-COOH) and the increase in ν_asym/sym(COO^-) pairs. The residual nitrile groups in HIPAN are converted into amides during hydrolysis and then into carboxyl. An indicator of this process is the decrease in -C≡N (≈2240 cm^{-1}) in FTIR, the increase in amide I/II (≈1650/1550 cm^{-1}) and COO^- compound (≈1570–1610/≈1390-1415 cm^{-1}). The H-bond structure (HIPAN -OH/-NH ↔ MDEA -OH/protonated amine) determines the broad absorption bands of 3600-3000 cm^{-1}. As MDEA increases, the H-bond network becomes stronger, broadening the bands and decreasing the frequency

(plural HIPAN): -COOH peak is clearer, -COO^- pair is slower, Δν is smaller; H-bonds are relatively weak; –C≡N is more noticeable than CN – lower level of hydrolysis/neutralization.

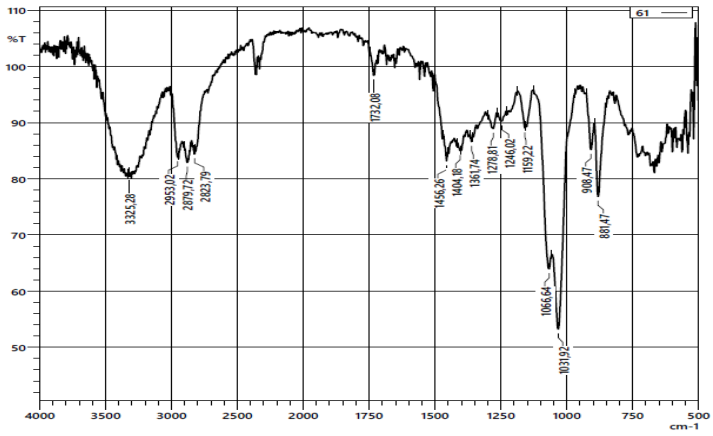

Figure 10 – IR spectra of HIPAN + triethanolamine (at a ratio of 1:9, HIPAN + TEA) (authors' materials)

In the IR spectrum of HIPAN+TEA, ν(OH) bands are broad, 3600-3000 cm^{-1}: curves that slope broadly and often downwards (to low frequency) due to the strong H-bonding of the three -CH_2CH_2OH groups in TEA and -OH/-NH/-COOH in HIPAN. As the proportion of TEA increases, these walking lines are expected to broaden and the maximum to move downwards (indicating increased H-bonding). ν(C-H) aliphatic, 2970-2870 cm^{-1}: The intensity increases slightly as the proportion of TEA increases. ν(C=O) free acid (-COOH), ~1715-1730 cm^{-1}: TEA deprotonated -COOH as a base -COO^-... H^+R_3N is coupled, so this peak weakens or almost disappears with excess TEA. ν_asym/ν_sym (-COO^-) carboxylate, ~1610–1570 / ~1415-1390 cm^{-1}: When the ammonium carboxylate pair is formed, the pair appears distinct and strong; An increase in δν = ν_asym − ν_sym indicates an increase in ionic character. Amide I (C=O), ~1680-1645 cm^{-1} and Amide II, ~1550±20 cm^{-1}: HIPAN depends on the level of hydrolysis; Amide II is sometimes covered around ν_asym -COO^-. ν(C≡N) residual PAN, ~2240-2245 cm^{-1}: decreases with increasing depth of hydrolysis. ν(C-O)/ν(C-N), 1260-1000 cm^{-1}: As TEA increases, broadening/strengthening of the C-O (alcoholic) and C-N ridges is expected in this fingerprint region (especially ~1150-1050 cm^{-1}).

3 RESULTS AND DISCUSSION

Experimental results showed that the optimal reaction conditions for polyacrylic acid, obtained from hydrolyzed polyacrylonitrile, with alkanolamine groups are a temperature of 40-45°C, a time of 6 hours, and a 1:9 feedstock ratio. The fact that virtually identical optimal conditions were obtained for all aminoalkanols is explained by the similarity of their chemical properties. The selection of feedstocks in a 1:9 ratio is also important, as excess alkanolamines also serve to improve the efficiency of grinding intensifiers.

Factors (temperature, time, feedstock ratio, etc.) influencing the optimal conditions for the synthesis of cement grinding intensifiers were studied. In the monoethanolamine-based synthesis, an 87% yield of the intensifier is obtained by conducting the reaction under optimal conditions for 6 hours. Further continuation of the reaction under these conditions leads to a decrease in the yield. This is due to the increased parallel reactions (such as cross-linking, decomposition, intermolecular interactions, etc.), which lead to a decrease in the intensifier's effect.

In synthesis using diethanolamine, the optimal component ratio is 1:9, and the optimal temperature is 60°C. Under these conditions, the intensifier yield is 90%. The highest yield is obtained with a 1:9 ratio of the initial products, but the effect (or quality) of the resulting intensifiers is low. Based on this, an optimal temperature of 45°C was chosen for intensifier production.

In synthesis using methyldiethanolamine, a 92% intensifier yield is obtained under optimal conditions within 6 hours. Further continuation of the reaction under these conditions leads to a decrease in yield. Thus, the optimal conditions for intensifier production are the reaction at 40°C for 6 hours, with a component ratio of 1:9. The product obtained under these conditions has a very good effect.

In synthesis using triethanolamine, the optimal component ratio is 1:9, and the optimal temperature is 45°C. Under these conditions, the intensifier yield is 87%. Therefore, the optimal temperature for producing the intensifier was 45°C.

The physicochemical and chemical properties of the resulting grinding intensifiers were determined experimentally.

Table 1
Main characteristics of the obtained intensifiers (authors' materials)

No.	Indicator	MEA-based	DEA-based	MDEA-based	TEA-based
1	Appearance	White powder	Liquid with a red tint	Liquid with a red tint	White powder
2	Density at 20°C, not less than	1.17	1.2	1.2	1.17
3	Water content, %, not more than	3.0	3.0	3.0	3.0
4	Hydrogen ion activity (pH), 2.5% aqueous solution	9.0 ± 1.0	9.0 ± 1.0	9.0 ± 1.0	9.0 ± 1.0
5	Chlorine ion content in dry matter, %, not more than	0.001	0.001	0.001	0.001
6	Solubility in water at 20°C, g/100 g of water	30	27	22	25

Physicochemical analysis of the resulting intensifiers revealed that all compositions exhibit a very strong C=O (amide) peak at 3300 cm^{-1}, a broad N-H elongation peak at 1236 cm^{-1}, and a strong C-N (amide III) elongation. These three peaks together confirm the clear presence of an amide group (-CONH-).

For grinding, clinker samples with a specific gravity of 3.15 from the cement manufacturer, Shymkent Cement Plant "Standartcement", were used.

Ball milling was performed using a laboratory ball mill with a standard ball load of approximately 20 kg.

To test the intensifiers in a laboratory ball mill, a particle size of less than 3.35 mm was required for the starting material. Therefore, the clinker and gypsum samples were pre-crushed using a cone crusher until 100% of the particles were 3.35 mm in size.

A clinker sample was fed into a ball mill operating at 70 rpm. After grinding, the samples were removed from the mill and analyzed for particle size distribution.

Table 2
Amount of intensifier required for grinding (authors' materials)

No.	Amount	Triethanolamine (TEA) (g)	G+M (g)	G+T (g)
1	0.05	0.52	0.58	0.51
2	0.25	2.51	2.60	2.63
3	0.50	5.04	5.12	5.11
4	1.00	10.54	10.05	10.67

Table 3
Particle size distribution (authors' materials)

No.	Intensifier	Concentration (%)			
1	Appearance	0.05	0.25	0.50	1.00
2	Without intensifier	42 μm	42μm	42μm	42μm
3	TEA	47 μm	45μm	56μm	57μm
4	G+T	41μm	38μm	44μm	44μm
5	G+M	46μm	38μm	38μm	47μm

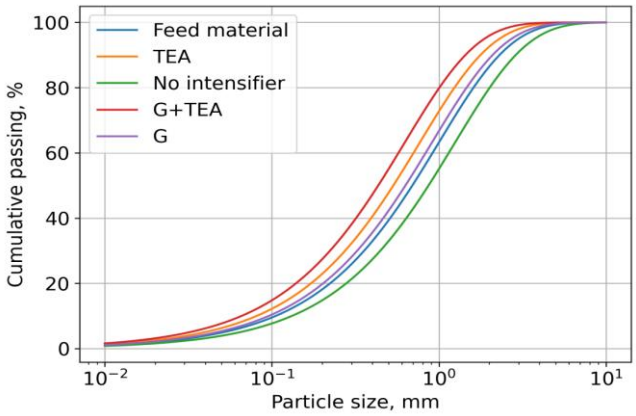

Figure 11 – Effect of grinding intensifier type and concentration on particle size distribution (authors' materials)

Figure 11, together with the data in Table 3, shows the effect of the type and dosage of additives activating the grinding process on the particle size distribution. Analysis of the results presented in Figure 11a shows that the introduction of the combined additive of G+TEA in an amount of 0.05% produces the smallest particles, for which the median diameter is d50 = 42 μm. This value is lower compared to the samples treated with 0.05% TEA and 0.05% G, where d50 is 47 and 46 μm, respectively. However, the overall degree of grinding remains low, since comparable particle sizes are also observed in the system without the use of additives. This effect is due to the extremely low concentration of the activator, insufficient to significantly influence the particle destruction process.

With an increase in the additive content to 0.25%, a clear shift in the total particle size distribution curves toward finer fractions occurs for both synthesized activators – G and G+TEA. In this case, the median particle size decreases to d50 = 38 μm, which is significantly smaller compared to the samples without additives and with TEA (d50 = 42 and 45 μm, respectively). It should be noted that the grinding products obtained using 0.25% G and 0.25% G+TEA are characterized by virtually identical particle size distributions. The addition of TEA at this concentration demonstrates lower efficiency.

The formation of finer particles in the presence of G and G+TEA additives is due to the synergistic effect between the active components of their formulations. The high basicity of HIPAN helps weaken the electrostatic interactions between particles, facilitating their disintegration during grinding. Alkanolamines, such as TEA and MDEA, with their lower basicity, primarily act as dispersants, preventing particle aggregation. The combined action of these components ensures a more stable and efficient grinding process.

According to the data presented in Figure 11c and Table 3, further increasing the dosage of TEA and G+TEA additives to 0.50% leads to an increase in the proportion of coarse fractions. Moreover, d50 values for systems with TEA vary in the range of 45-56 μm, while for G+TEA they are 38-44 μm. Increasing the G additive concentration to 0.5% does not significantly change the particle size distribution; however, the resulting product remains finer compared to the material without additives.

Excessive amounts of grinding activators alter the surface properties of particles, promoting their adhesion to each other. Higher additive dosages alter the surface charge and degree of hydration of particles, enhancing agglomeration processes. Furthermore, the presence of amino groups ($-NH_2$) in HIPAN and ethylamine fragments ($-CH_2CH_2NH_2$) in TEA leads to the adsorption of polar functional groups on the particle surface, increasing their hydrophilicity and, consequently, interparticle attraction. A similar trend persists even with increasing additive concentrations to 1.0%. The development of agglomeration processes limits further particle size reduction by reducing the effective surface area available for grinding.

4 CONCLUSIONS

1. A literature review revealed that alkanolamines are effective raw materials for synthesizing grinding intensifiers. However, the compatibility of the resulting cement product with various chemical additives (currently widely used polycarboxylates) was not fully studied.

2. A literature review and study of raw material sources in the Republic of Kazakhstan identified the best raw materials for grinding intensifiers: methyldiethanolamine, a gas processing waste product, and hydrolyzed polyacrylonitrile (HIPAN), obtained from recycled nitrofiber.

3. The efficiency of a method for purifying methyldiethanolamine, a waste product of the natural gas purification process, was studied using IR spectroscopy, chromatography, and mass spectrometry. The purity of the purified methyldiethanolamine (MDEA) was found to be very high, and the proposed method demonstrated high efficiency.

4. It was found that adding alkanolamines to the mixing water leads to the formation of additional monosulfate aluminate (MSA) and C-S-H in the order DEA, DIPA < TEA < TIPA, which is similar to the order of initial dissolution rates and cumulative heat of reaction R_3. The effect was less pronounced when using alkanolamines as grinding intensifiers, since the amount of alkanolamine was approximately halved.

5. It was determined that the cumulative distribution curve of the product obtained with the addition of 0.25% of both synthesized grinding intensifiers, G+M and G+T, shifts toward finer grinding due to the unique combination of active components (alkanolamines, HIPAN), which allows them to act synergistically. HIPAN provides increased efficiency due to its high basicity, which reduces the electrostatic attraction between particles, resulting in finer grinding and increased productivity. In contrast, alkanolamines (TEA, MDEA) have lower basicity and act as dispersants, helping to keep particles separated. When used together, HIPAN and alkanolamines complement each other, increasing grinding efficiency and product stability.

6. This research was conducted as part of the research project AP26102705 “Development and Production of Cement Grinding Intensifiers Based on Local Raw Materials”, funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan.

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