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Optimization of Acidic Pickling Wastewater Neutralization using $Ca(OH)_2$ and KOH Blending in Petroleum Production Facilities in the Niger Delta.

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ABSTRACT
Water pollution in the petroleum industry is a rampant issue that is deadly to marine life, livestock and human welfare. The drilling, fracking and pickling of metal operations result in hazardous wastewater that demands robust wastewater treatment. The processing of acidic metal pickling effluents is an issue in operations. This investigation deals with a dual reagent neutralization experiment to treat our wastewater using a blend of Potassium Hydroxide (KOH) and Calcium Hydroxide ($Ca(OH)_2$) at various ratios. Each mixture's stoichiometric efficiency, sludge quality and cost are compared. Our findings have illustrated that a 60:40 $Ca(OH)_2$ to KOH ratio yields the greatest economic trade-off when dealing with sludge reduction. We have found optimal conditions by which the solution would remain within sufficient residence time, from 15- 20 minutes and pH level, 6.95 to 7.05 to precipitate all the heavy metal complexes. This provides a scalable framework for the betterment of oil wastewater treatment between upstream and downstream operations.

Keywords: *Pickling Waste; Neutralization; Petroleum Production; Sludge Optimization; Total Dissolved Solids; Total Titratable Acidity; Solubility Product Constant; Sludge Volume Index*

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I. INTRODUCTION

In the petroleum industry acid cleaning and pickling are employed to remove oxide scale, corrosion products and mineral deposits from metallic equipment and process components, including pipelines, flowlines, heat exchangers and storage vessels. The composition of the cleaning solution depends on the material being treated and the nature of the deposits (Lochyński et al., 2021). Hydrochloric acid (HCl) is commonly used for steel pickling, whereas mixtures of nitric acid (HNO) and hydrofluoric acid (HF) are particularly associated with the pickling of stainless steels and other corrosion resistant alloys (Ghare et al., 2013). Consequently, spent acidic cleaning and pickling liquors may contain residual acids and dissolved metals released from the treated surfaces. Iron (Fe) is regularly found in used acid pickling liquids and sometimes Cr and Ni also present when stainless steel and other metals made of alloys pickling is performed. These concentrations and species will change, however depending on alloy nature, acid type and compositions their conditions and amount of metal dissolved (Ghare et al., 2013). From pickling of stainless steels, chromium containing compounds comprise the major phase in the produced sludge and iron and chromium phases found in residues from sulfuric and both nitric and hydro fluoric acid pickling systems (Ito et al., 1998). Acid pickling wastewater contains a significant level of residual acidity and dissolved metals has to be properly managed either through discharge or reuse. Since heavy metals contained within effluent discharges remain persistent and are not typically degraded by treatment with biological methods, there has been considerable interest in reducing the amount of those. They may accumulate over time in other organisms, leading to toxic-induced effects even if they remain in relatively lower concentration level in environments. Neutralization is one of the most established approaches for treating acidic industrial wastewater, particularly effluents generated from metal finishing and pickling operations (Agrawal et al., 2006; Dahlgren, 2010). The process involves the addition of an alkaline reagent to increase the wastewater pH, thereby promoting the formation and precipitation of sparingly soluble metal hydroxides (Snoeyink & Jenkins, 1980). Calcium hydroxide [Ca(OH)], commonly referred to as hydrated or slaked lime, has been widely used as a neutralizing agent because of its relatively low cost, availability and effectiveness in increasing pH and promoting metal precipitation. Despite these advantages, conventional lime neutralization has limitations. The relatively low solubility and dissolution rate of Ca(OH) can restrict the rate at which alkalinity is supplied to acidic wastewater, while the precipitation behavior of individual metals varies substantially with

pH. Consequently, simultaneous removal of multiple dissolved metals may require careful control of the neutralization conditions. These limitations have encouraged studies towards alternative alkaline agents and process optimization and recovery strategies to remove acidic industrial effluents from wastewater (Mani et al., 1988; Morya et al., 2022). Additionally, chemical precipitation is a considerable physiochemical removal mechanism; as pollutants dissolved in water are converted to insoluble precipitates and can then be isolated by the techniques of settlement, clarify and filtration (Lin et al., 2022). Hydroxide precipitation is highly sensitive to pH due to metal hydroxides having differences in their insolubilities based on pH and metals. Thus, precise pH control is essential for maximizing metal removal while meeting applicable discharge requirements (Ezzeddine et al., 2015). Previous studies have demonstrated the importance of alkaline neutralization in the treatment of acidic, metal containing industrial effluents (Nemerow & Dasgupta, 1991; Zinck & Aubé, 2000). Lime and other alkaline reagents, including sodium carbonate and caustic soda, can be employed to increase the pH of acidic wastewater and promote metal hydroxide precipitation. However, the optimum precipitation pH differs among metals, meaning that a pH suitable for removing one metal may not necessarily provide maximum removal of another. Furthermore, the relatively slow dissolution of lime may limit the kinetics of neutralization, particularly when treating highly acidic wastewater. Accordingly, there is a need to investigate neutralization systems that can combine the economic and practical advantages of Ca(OH) with improved reaction kinetics. In this study, a blended Ca(OH) :KOH system is investigated for the treatment of acidic pickling wastewater. The addition of KOH is intended to provide a more readily soluble source of alkalinity, thereby accelerating pH adjustment and potentially enhancing metal hydroxide precipitation, while Ca(OH) provides the economic advantage associated with lime based neutralization. The study therefore evaluates the potential of the Ca(OH) :KOH blend to improve neutralization performance and dissolved metal removal while maintaining the economic feasibility of conventional lime treatment. This approach provides a basis for assessing whether mixed alkali neutralization can offer an effective alternative for the treatment of acidic pickling wastewater.

II. Literature Review

Pickling is the chemical treatment of metal surfaces to remove oxides and scale which generates highly acidic wastewater, typically with a pH below 1.0 and elevated concentrations of multivalent metals such as iron, chromium and nickel (Charazińska et al. 2022). This acidic wastewater is toxic and endangers aquatic ecosystems if the wastewater is not stabilized properly. Xu et al. (2022) noted that the increasing of tough emission standards is difficult to handle without further treatment in particular on the acid pickling sludge. A treatment is presented by Jarnerud et al. (2021) by which wastes rich in CaO namely fly ash and the calcined lime mud neutralizes steel plant acid wastewater and decrease content of most heavy metals Cr, Fe, Ni, Mo, and Zn in the Wastewater. This means that immobilization techniques must be deployed to keep leaching levels below the limits set by law. Calcium hydroxide (Ca(OH)), or hydrated lime, has long been the best way for factories to control acidity. Lee et al. (2023) observe that while lime is valued for its low cost and high availability, it is a significant contributor to secondary waste generation. Specifically, the reaction between Ca(OH) and sulfate rich acids produces large volumes of gypsum based sludge. The sludge often exhibits poor settling characteristics and high operational costs due to high water retention and the handling of voluminous byproducts (Lee et al., 2023). Potassium hydroxide (KOH) as an alternative to lime offers distinct thermodynamic advantages. Unlike the relatively insoluble lime, KOH dissociates instantaneously, providing rapid pH adjustment. Binnemans & Jones (2024) demonstrate that strong bases are essential for cleaner production pathways where high purity neutralization is required to prevent the resolubilization of amphoteric metals. However, the high cost of KOH prevents its standalone use in large scale petroleum operations. Also, the high solubility of potassium salts can lead to elevated Total Dissolved Solids (TDS) in the final effluent, a parameter that Murodjon et al. (2020) identify as a critical constraint in brine management systems. The integration of both CA(OH) and KOH into a single treatment regimen is theorized to provide a synergistic effect that addresses the limitations of both reagents. In such blended systems, the CA(OH) particles serve as nucleation sites for the formation of denser, more crystalline metal hydroxide flocs, while the KOH component provides immediate hydroxyl availability for rapid neutralization. Xu et al. (2022) suggest that altering the reagent matrix can significantly improve the Sludge Volume Index (SVI), thereby reducing the overall volume of hazardous waste for disposal. This study introduces a novel hybrid neutralization approach specifically for petroleum pickling wastewater, quantifying optimal Ca(OH) /KOH blend ratios and provide a framework for industrial application, which is a unique contribution to the field. While the literature extensively discusses the individual properties of CA(OH) for steel mill waste (Woodrow et al., 2001) and KOH for specialized chemical processes (Zhang, 2023), there is a notable paucity of data regarding their optimized blending ratios specifically for petroleum production pickling waste. Current industrial practices often rely on trial and error dosing. Singhal et al. (2006) demonstrate that the most economically viable neutralization strategy is determined by the intersection of chemical reagent costs and sludge disposal fees, favoring a blended Ca(OH) /NaOH system over traditional lime only methods. As established by Elchemy (2026), traditional neutralization relying solely on lime is cost effective but produces expensive to manage, gypsum rich sludge, whereas pure KOH

offers high reactivity at a prohibitive cost. This study addresses this gap by quantifying the stoichiometric requirements and sludge reduction potential of a CA(OH) and KOH hybrid system. This study investigates the synergy of Ca(OH) and KOH in treating petroleum pickling wastewater so as to improve the settling rate of precipitates and minimize total chemical consumption. Based on the experimental results, an optimal combination ratio was selected to enhance sludge settling while minimizing chemical consumption, thereby achieving a balance among treatment efficiency, operational cost and environmental sustainability under field scale conditions.

III. MATERIALS AND METHODS

3.1 Materials

The materials used in this study were selected based on their chemical purity and relevance to industrial scale up in petroleum operations. Chemical reagents came from the GGI Laboratory in Port Harcourt, Nigeria. All solutions were prepared using deionized water to ensure precise results. The materials listed were used properly in the experiment.

1. 15 ml Pipette
2. pH Meter
3. 50 ml Burette
4. Retort stand
5. 38.08 ml of Hydrochloric acid (8% HCl, standardized to 0.1N)
6. 10 ml of Potassium hydroxide (KOH), 0.1 N laboratory grade
7. 15 ml of Calcium hydroxide Ca $(OH)_2$ analytical grade
8. 1000 ml of de ionised water
9. Phenolphthalein Indicator
10. Volumetric flask
11. Magnetic stirrer
12. Weighing balance
13. Beaker
14. Burner

3.2 Methods

A 0.1 N alkaline stock of potassium hydroxide (KOH) was made by dissolving laboratory grade anhydrous pellets in a measured amount of solvent. The KOH showed high solubility and a strong heat release during dissolution, which led to its quick and complete breakdown into K^+ and OH ions at room temperature. At the same time, a calcium hydroxide Ca $(OH)_2$) solution was created by adding 1.85 g of the reagent into a 500 ml volumetric flask. Because calcium hydroxide has a low solubility product (ksp) in water, the mixture required a magnetic stirrer to rotate at a constant speed of 500 rpm for a long time. This stirring was essential to overcome the compound's lattice energy and create a stable, uniform solution for blending. To optimize reaction kinetics during the neutralization phase, an 8% Hydrochloric Acid (HCl) solution was used as a catalyst. This specific concentration was derived through stoichiometric calculations to lower the activation energy required for the neutralization process. The addition of the HCl catalyst was intended to facilitate a more rapid proton exchange between the acidic pickling waste and the alkaline blend, thereby improving the operational efficiency of the treatment process in petroleum production settings.

3.3 Characterization of Pickling Wastewater

3.3.1. Chemical Composition and Acid Load

Petroleum production pickling wastewater usually contained high amount of mineral strong acid generated from acidic cleaning and pickling descaling operations. The principal acidic constituents are generally hydrochloric acid (HCl) and sulfuric acid (H SO), which amounts in pickling descaling water were vary in different pickling process and operational conditions, and their ratio varied also depends on operation conditions. In addition to residual free acids, the wastewater typically contains substantial concentrations of dissolved metal ions and their corresponding salts, particularly iron(II) chloride (FeCl), which is generated through the dissolution of metallic oxides and corrosion products during the pickling process. Other dissolved constituents, such as trace metals and suspended solids, may also be present, further increasing the chemical complexity and corrosivity of the wastewater. Comprehensive characterization of the wastewater was undertaken before the neutralization experiments to establish its acid strength and determine the appropriate dosage of the alkaline neutralizing agents. The primary parameter evaluated was the Total Titratable Acidity (TTA), which represents the total acid neutralizing capacity of the wastewater. Total Titratable Acidity encompasses both the concentration of free hydrogen ions (H) originating from unreacted mineral acids and the acidity associated with hydrolyzable or acid generating dissolved metallic salts present in the solution.

Consequently, TTA provides a more representative measure of the overall acidity of the wastewater than pH alone, as pH reflects only the instantaneous hydrogen ion activity rather than the total acid load requiring neutralization. The determination of TTA served as the basis for calculating the stoichiometric quantity of alkaline reagent necessary to achieve complete neutralization of the wastewater. The measured acidity values were subsequently used to establish the volume and concentration requirements of the potassium hydroxide (KOH) and calcium hydroxide [Ca(OH)] binary alkaline blends employed in this study. Accurate quantification of TTA was therefore essential for optimizing reagent dosage, minimizing excessive alkali consumption and and evaluating the neutralization performance of the different alkaline blend ratios investigated for the treatment of petroleum production pickling wastewater.

3.3.2. Quantitative Analysis by Standard Titration

To quantify the acidity, a standard potentiometric or indicator based titration is employed. The method follows the ASTM standards for water quality analysis:

1. Initial pH measurements are taken using a calibrated digital pH meter to establish the baseline acidity, which typically falls within the range of 0.5 to 2.0 for untreated pickling liquor.
2. A known volume of the wastewater Va is titrated against a standard base 0.1 N KOH or the prepared alkaline blend. The reaction follows the fundamental neutralization equation:

$$H^{+}_{(aq)} + OH_{(aq)} \longrightarrow H_2O$$

3. The titration reaches its conclusion when the moles of the base added are chemically equivalent to the moles of the acid present in the wastewater. In this study, the transition from an acidic to a neutral state is visually confirmed by the change in a phenolphthalein indicator or the stabilization of the pH at approximately 7.0.

3.3.3. Indicators of Neutralization Efficiency

The characterization process defines efficiency based on the volume of the neutralizer consumed. In high volume petroleum production, a high efficiency neutralizer is characterized by:

1. The ability to neutralize the waste using the smallest possible quantity of reagent.
2. The stability of the final pH to prevent acidic rebound, which can occur if the wastewater contains complexed metal ions that hydrolyze over time.
3. Characterization also involves observing the formation of sludge, such as $CaSO_4$ or metallic hydroxides, which must be managed following the neutralization of the aqueous phase.

3.4 EXPERIMENTAL PROCEDURE

3.4.1 Titrimetric Analysis Setup

Spent pickling wastewater samples were collected from a petroleum maintenance facility where acidic pickling operations are routinely conducted for the cleaning and descaling of metallic equipment. Immediately after collection, the wastewater samples were transferred into clean, chemically resistant polyethylene containers, tightly sealed to prevent contamination and changes in chemical composition during transportation. The samples were transported to the laboratory and stored under appropriate conditions before analysis and subsequent neutralization experiments. Before each experimental run, the wastewater was thoroughly homogenized to ensure representative sampling. The neutralization experiments were conducted in a laboratory scale, 2 L stirred tank reactor equipped with a mechanical agitator to provide continuous and uniform mixing throughout the reaction period. The reactor configuration was selected to simulate the hydrodynamic conditions commonly encountered in industrial wastewater neutralization processes while ensuring adequate contact between the acidic wastewater and the alkaline neutralizing agents. The agitation speed was maintained at a constant value throughout each experiment to minimize concentration gradients and promote rapid acid base interactions. The neutralization capacity of the selected alkaline reagents, potassium hydroxide (KOH) and calcium hydroxide [Ca(OH)], was initially evaluated through a standard forward acid base titration procedure. A conventional titration assembly was employed, comprising a retort stand fitted with a calibrated burette containing the standardized hydrochloric acid (HCl) solution as the titrant. Before each titration, the burette was thoroughly rinsed with the acid solution and filled carefully to eliminate air bubbles and ensure accurate volume measurements. Initial burette readings were recorded before the commencement of each experiment. For each experimental trial, a 25 mL aliquot of the prepared alkaline solution was accurately measured using a Class A volumetric pipette and transferred into a clean 250 mL Erlenmeyer (conical) flask. To facilitate endpoint detection, two to three drops of phenolphthalein indicator were added to the alkaline solution. The addition of the indicator produced a distinct pink coloration, confirming the alkaline nature of the solution prior to neutralization. The prepared sample was then positioned beneath the burette and continuously agitated during titration to ensure homogeneous mixing and complete interaction between the acid titrant and the alkaline

solution. This experimental arrangement provided a reliable and reproducible means of evaluating the neutralization characteristics of the individual alkaline reagents before their application in the treatment of petroleum production pickling wastewater.

3.4.2 Titration Protocol

The standard acid solution was delivered from the burette into the alkaline solution in a controlled, dropwise manner while the reaction mixture was continuously swirled to ensure thorough mixing and uniform distribution of the titrant. As the endpoint approached, the acid was added more cautiously, one drop at a time, to prevent overshooting the equivalence point. The titration was continued until the indicator exhibited a distinct and permanent color transition from pink to colorless, signifying complete neutralization of the hydroxide ions and the attainment of the equivalence point. Following the endpoint determination, the final burette reading was recorded and the volume of acid consumed during the titration was calculated as the difference between the initial and final burette readings. Each titration was repeated in independent trials to improve the precision and reproducibility of the experimental results and concordant titre values were obtained where applicable. The entire procedure was conducted separately for the pure potassium hydroxide (KOH) solution and the pure calcium hydroxide [Ca(OH)] solution. The results obtained from these individual titrations served as baseline data for evaluating the neutralization characteristics and efficiency of each alkaline solution before subsequent comparative analyses.

3.4.3 Formulation of Alkaline Blends

To evaluate the synergistic neutralization performance of a binary alkaline system, aqueous solutions of potassium hydroxide (KOH) and calcium hydroxide [Ca(OH)] were prepared and combined in predetermined volumetric proportions. The binary blends were formulated at KOH(OH) ratios of 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100, thereby covering the full compositional range from the individual alkaline reagents to their intermediate mixtures. These blending ratios were selected to systematically assess the influence of reagent composition on the overall neutralization efficiency and to identify any synergistic interactions arising from the combined use of the two alkaline reagents. For each experimental run, the total volume of the blended alkaline solution was maintained at 25 mL to ensure consistency across all titration experiments. The required volumes of each reagent were measured using calibrated volumetric pipettes and transferred into a clean conical flask before gentle mixing to obtain a homogeneous solution. For example, the 60:40 blend consisted of 15 mL of KOH solution and 10 mL of Ca(OH) solution, while the remaining blend compositions were prepared in a similar manner by adjusting the respective volumes of the individual alkaline solutions without altering the total sample volume. Each binary alkaline mixture was subsequently subjected to the standardized acid base titration procedure described in Section 3.5.2. During titration, the acid titrant was introduced gradually under continuous agitation until a permanent endpoint, indicated by the prescribed indicator color change, was achieved. The initial and final burette readings were recorded and the corresponding titre values were determined for each blend. To improve analytical precision and reproducibility, all experiments were performed in independent replicates and concordant titre values were used for subsequent analysis. The experimental data generated from the different blending ratios were compared to evaluate the neutralization capacity of each binary alkaline formulation. The results were further analyzed to determine the optimum Ca(OH) :KOH mixing ratio capable of achieving the highest neutralization efficiency for petroleum production pickling wastewater. This systematic evaluation also provided insight into the potential synergistic interactions between the two alkaline reagents and their suitability for application in wastewater treatment processes.

IV. RESULT AND DISCUSSION

The research reports that the final treated water reached a pH close to neutral, approximately 6.95–7.05. It also states that increasing the KOH fraction improved the effectiveness of neutralization, while reducing the proportion of Ca $(OH)_2$ increased the volume of acid required to reach the endpoint. It concludes that KOH is more effective but Ca $(OH)_2$ is cheaper, so the blend offers a practical compromise. Table 1 and Figure 1 present the titration results obtained for different binary mixtures of calcium hydroxide [Ca(OH)] and potassium hydroxide (KOH) used as neutralizing agents. Six blend ratios were evaluated, ranging from 100% Ca(OH) to 100% KOH, with three independent titration trials performed for each formulation. The average titre values were calculated to assess the relative neutralization capacity of each alkaline blend. The results demonstrate that the average volume of hydrochloric acid (HCl) required for neutralization varied only slightly across the different alkaline compositions, ranging from 19.50 mL to 21.50 mL. The 100% Ca(OH) formulation recorded an average titre of 20.10 mL, indicating its inherent neutralization capacity when used as the sole alkaline reagent. In contrast, the 100% KOH formulation required the highest average acid volume (21.50 ml), suggesting a greater concentration of readily available hydroxide ions in solution and consequently, a higher neutralization capacity. Among the binary mixtures, the 60:40 Ca(OH) :KOH blend exhibited the

lowest average titre value (19.50 mL). This reduction in acid consumption indicate that this blend achieved a more efficient neutralization reaction under the experimental conditions. The observation suggests the possibility of a synergistic interaction between Ca(OH) and KOH, whereby the combined reagents enhanced the utilization of hydroxide ions compared with the individual reagents alone. As the proportion of KOH increased beyond 40%, the average titre values gradually increased from 19.90 mL for the 40:60 blend to 21.10 mL for the 20:80 blend and finally 21.50 mL for pure KOH. This trend is consistent with the higher solubility and complete dissociation of KOH in aqueous solution, which provides a greater concentration of available OH ions than Ca(OH) . Consequently, higher volumes of acid were required to achieve the titration endpoint for mixtures containing larger proportions of KOH. The replicate trials for each formulation exhibited only minor variations, generally within ±0.5 mL of the mean value. This low level of variability indicates good repeatability of the titration procedure and demonstrates that the experimental methodology produced consistent and reproducible results. Overall, the findings indicate that all Ca(OH) :KOH blends possessed effective neutralization capacity, with only slight differences among the formulations. The 60:40 Ca (OH) : KOH blend produced the lowest average titre value and therefore represents the most promising blend based on acid consumption alone.

Table 1. Composition of Ca(OH) -KOH Blends Used for Pickling Wastewater Neutralization

Component/Trial	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
$Ca(OH)_2$ (%)	100.0	80.00	60.00	40.00	20.00	0.000
KOH (%)	0.000	20.00	40.00	60.00	80.00	100.0
Trial 1	19.50	20.90	19.00	19.60	21.00	21.00
Trial 2	20.50	20.10	20.00	20.00	21.00	22.00
Trial 3	20.30	20.02	19.50	20.10	21.20	21.50
Average	20.10	20.40	19.50	19.90	21.10	21.50

Table 2 and Figure 2 show the influence of Ca(OH) :KOH blending ratios on the neutralization characteristics of the alkaline system. The performance of the six formulations was evaluated using the average titration response, hydrochloric acid (HCl) consumption and the final pH after neutralization. The results demonstrate that varying the Ca (OH) :KOH ratio significantly affected the alkalinity behavior and acid neutralizing performance of the binary blends. The average titration results for the alkaline formulations ranged from 19.50 ± 0.02 mL to 21.50 ± 0.40 mL. Among the investigated blends, Sample 3 (60:40 Ca(OH) :KOH) exhibited the lowest titration value (19.50 ± 0.02 mL), whereas Sample 6 (0:100 Ca(OH) :KOH) recorded the highest value (21.50 ± 0.40 mL). The observed variation indicates that the proportion of KOH within the binary mixture influenced the availability of reactive hydroxide species during titration. The higher titration response observed for KOH rich formulations attributed to the high aqueous solubility and complete dissociation of KOH, which provide a greater concentration of freely available hydroxide ions compared with Ca(OH) . Calcium hydroxide contributes alkalinity through dissolution according as shown in Equation (1)

(1)

However, its relatively low solubility limits the immediate release of hydroxide ions into solution. Conversely, potassium hydroxide undergoes complete dissociation resulting in rapid hydroxide availability as shown in Equation (2)

(2)

Therefore, increasing the KOH fraction from Sample 1 (100:0) to Sample 6 (0:100) enhanced the apparent alkalinity of the blends, as reflected by the gradual increase in the titration response. The HCl consumption values followed a similar pattern, increasing from 0.022 ± 0.002 mL for Sample 3 to 0.140 ± 0.008 mL for Sample 6. The highest acid requirement observed for the pure KOH formulation confirms its greater neutralization potential due to the availability of dissociated hydroxide ions. In contrast, Sample 3 required the lowest amount of HCl, suggesting that the 60:40 Ca(OH) :KOH formulation achieved effective acid neutralization with reduced acid demand. This behaviour indicates that the combination of Ca(OH) and KOH may provide a complementary alkaline effect, where KOH enhances immediate hydroxide availability while Ca(OH) provides sustained alkalinity through gradual dissolution. The intermediate formulations also demonstrated favourable neutralization characteristics. Samples 1 and 2, containing higher proportions of Ca(OH) , produced titration values of 20.10 ± 0.30 mL and 20.40 ± 0.25 mL, respectively, indicating that calcium hydroxide alone and calcium hydroxide rich blends possess considerable neutralization capacity despite their lower solubility. Sample 4 (40:60 Ca(OH) :KOH) produced a titration value of 19.90 ± 0.30 mL,

suggesting that increasing KOH beyond the optimum blend ratio did not proportionally improve the neutralization response. The final pH values obtained after treatment ranged from 6.950 to 7.050, demonstrating that all alkaline formulations successfully achieved near neutral conditions. Sample 3 produced a final pH of 7.000, which represents the ideal neutralization endpoint. The narrow pH variation of only 0.10 units among all treatments indicates that the alkaline blends provided effective control of acidity and that the titration procedure was reproducible. Although KOH rich blends produced slightly higher final pH values (7.030–7.050), these differences remain within the acceptable neutral range and may not represent a significant practical advantage. The low standard deviations associated with both titration results and HCl consumption demonstrate good experimental precision. Sample 3 exhibited particularly high reproducibility, with a standard deviation of only ±0.02 mL, indicating consistent performance across replicate measurements. This suggests that the 60:40 Ca(OH) –KOH blend provided a stable and predictable neutralization response under the experimental conditions. The results indicate that the binary alkaline system exhibited composition dependent neutralization behaviour. Although pure KOH (Sample 6) demonstrated the highest titration response and acid consumption, the 60:40 Ca(OH) :KOH blend (Sample 3) provided the most balanced performance by achieving a neutral endpoint (pH 7.000) while requiring the lowest HCl consumption (0.022 ± 0.002 mL). The improved performance of Sample 3 is attributed to the synergistic contribution of both alkaline components, where KOH provides rapid hydroxide release and Ca(OH) enhances sustained alkalinity. Therefore, the 60:40 Ca(OH) –KOH formulation can be considered the most promising blend for further evaluation in petroleum pickling wastewater neutralization applications.

Table 2. Neutralization Performance of Binary Alkaline Blends

Sample	$Ca(OH)_2$: KOH Blend ratio	Average Titration Result (ml)	HCl Consumption (mL)	Final pH
1	100:0	20.10 ± 0.30	0.038 ± 0.004	6.950
2	80:20	20.40 ± 0.25	0.040 ± 0.003	6.970
3	60:40	19.50 ± 0.02	0.022 ± 0.002	7.000
4	40:60	19.90 ± 0.30	0.032 ± 0.004	7.010
5	20:80	21.10 ± 0.35	0.080 ± 0.006	7.030
6	0:100	21.50 ± 0.40	0.140 ± 0.008	7.050

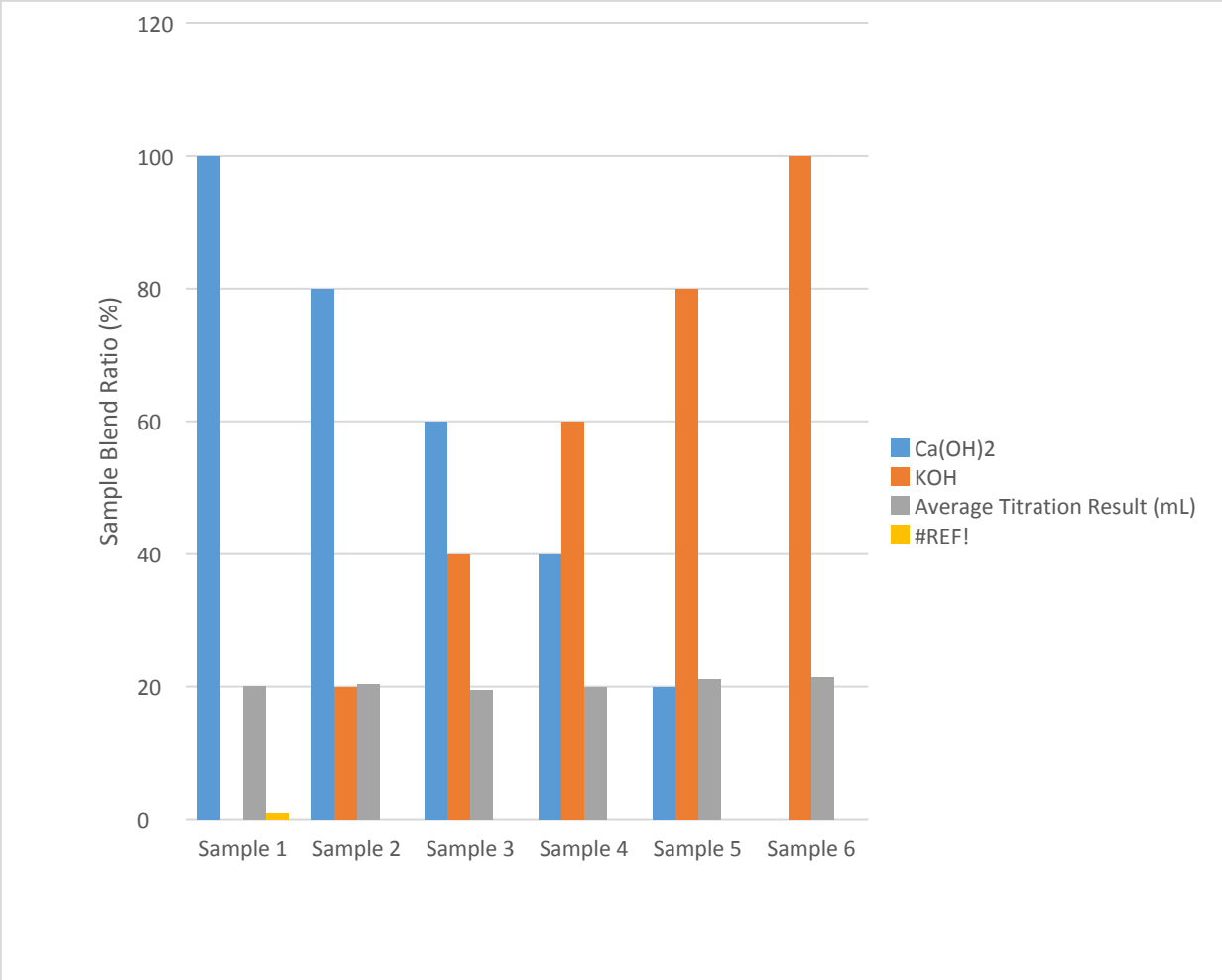

Figure 1: Effect of Ca(OH) :KOH blend ratio on neutralization efficiency

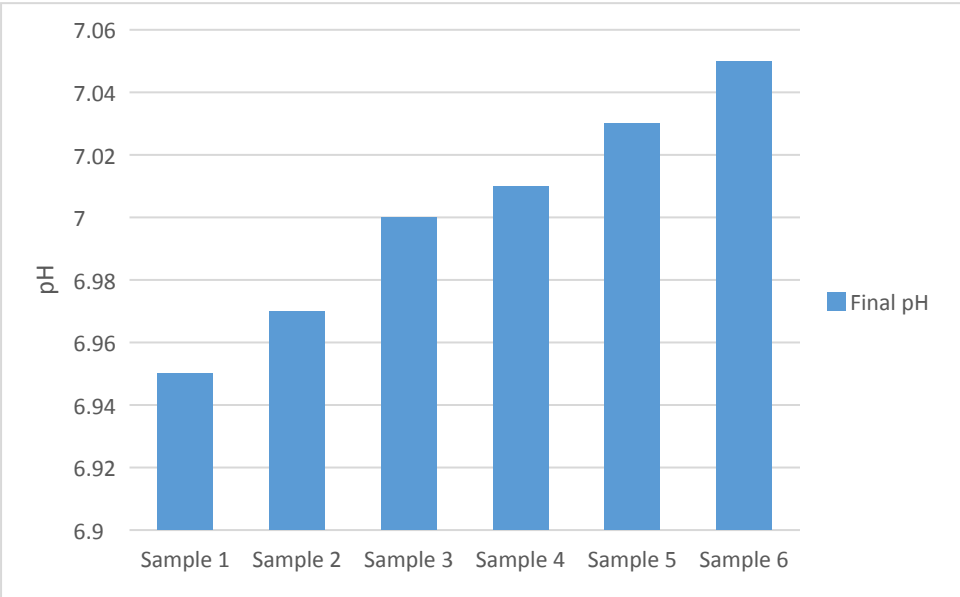

Figure 2: pH of the Pickling Wastewater after Neutralization.

The experimental results demonstrate a clear correlation between alkali solubility and neutralization kinetics, reinforcing the fundamental chemical principle that higher dissociation constants lead to more rapid pH adjustments in acidic streams, as illustrated in Figure 3. The rapid endpoint observed with Potassium Hydroxide

(KOH) is directly attributable to its high solubility and complete dissociation in aqueous environments. In contrast, calcium hydroxide (Ca(OH)), while functionally effective, exhibits slower reaction rates due to its limited solubility (Lewis & Boynton, 1995). This disparity implies that KOH provides near instantaneous reactivity, which is critical for systems with high flow rates, whereas $Ca(OH)_2$ requires extended contact time to achieve equivalent pH stabilization. These findings align with the broader literature (Chen et al., 2005), where the choice of reagent typically rests on a trade off between the low commodity cost of lime and the operational precision of caustic reagents. A central argument of this study is the shift toward a blended neutralization system that integrates a partial substitution of KOH into a primary $Ca(OH)_2$ process. This hybrid approach addresses the trade offs identified by Zinck and Aubé (2000), specifically balancing capital expenditure such as the size of neutralization tanks against operational expenditure. By leveraging the rapid reaction speed of KOH alongside the high buffering capacity and cost effectiveness of $Ca(OH)_2$, a blended system allows for a smaller equipment footprint due to faster residence times without the prohibitive expense of a pure KOH treatment. This provides a mid point for facilities that require moderate complexity but demand optimized reaction speeds.

In practical terms, the study suggests that production engineers can improve wastewater treatment by using a partial KOH substitution instead of relying entirely on $Ca(OH)_2$. This strategy facilitates faster neutralization and higher throughput in existing infrastructure while potentially reducing the volume of gypsum based sludge typically generated by pure lime neutralization. Furthermore, KOH can be utilized as a fit reagent for fine pH adjustments while $Ca(OH)_2$ handles the bulk acidity, ensuring tighter compliance with environmental discharge permits. Ultimately, the integration of these reagents confirms that while $Ca(OH)_2$ is economically superior for bulk neutralization, its kinetic limitations pose risks to process efficiency that are best mitigated through a pragmatic, blended model.

V. Conclusion

This study confirms that a blended neutralization model, using a combination of calcium hydroxide ($Ca(OH)_2$) and potassium hydroxide (KOH), effectively bridges the gap between cost efficiency and operational performance in petroleum wastewater treatment. While lime remains economically superior for bulk acidity neutralization, its inherent kinetic limitations, specifically its slow dissolution rate and the production of bulky sludge are successfully mitigated through partial KOH substitution. The implementation of this hybrid approach significantly reduces residence time, making it highly suitable for high throughput industrial systems that require rapid processing. Furthermore, the dual reagent system provides robust management of fluctuating acid loads, ensuring that effluent pH remains within regulatory limits despite variations in influent chemistry. By leveraging the settling benefits of calcium based flocs alongside the high reactivity of KOH, the process optimizes sludge management, leading to denser precipitates and potentially lower disposal costs. Ultimately, these findings provide a scalable and scientifically grounded framework for enhancing the efficiency of environmental remediation strategies within both upstream and downstream petroleum operations.

4. Contributions to Knowledge

The contributions of this study to the field of industrial wastewater management are summarized across theoretical, practical and educational areas:

1. The study establishes a predictive framework for hybrid alkali interactions in oilfield wastewater.
2. It offers a low cost operating option specifically for oilfield wastewater treatment, demonstrating how partial reagent substitution can meet environmental standards without excessive expenditure.
3. It Provides a decision making matrix for production engineers to balance reagent costs against reaction kinetics.
4. It offers a scalable and laboratory validated model for petroleum environmental remediation.

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