The Synthesis of Calcium Salt from Brine Water by Partial Evaporation and Chemical Precipitation

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Abstract. In this study would be investigated the effects of partial evaporation and chemical precipitation in the formation of calcium salt from brine water resources. The chemical reagents used in the study was oxalate acid (C₂H₂O₄)₃, ammonium carbonate (NH₄)₂CO₃ and ammonium hydroxide (NH₄OH) with reagent concentration of 2 N, respectively. The procedure was 10 liters brine water evaporated until 20% volume and continued with filtration process to separate brine water filtrate from residue (salt). Salt resulted from evaporation process was characterized by Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) techniques. Filtrate then was reacted with C₂H₂O₄, (NH₄)₂CO₃ and NH₄OH reagents to get salt products in atmospheric condition and variation ratio volume brine water/chemicals (v/v) [10/1; 10/5; 10/10; 10/30; 10/50; 20/1; 20/5; 20/10; 20/20; 20/30; 20:50]. The salt product than were filtered, dried, measured weights and finally characterized by SEM/EDS and XRD techniques. The result of experiment showed the chemical composition of brine water from Tirta Sanita, Bogor was 28.87% Na, 9.17% Mg, 2.94% Ca, 22.33% O, 0.71% Sr, 30.02% Cl, 1.51% Si, 1.23% K, 0.55% S, 1.31% Al. The chemical composition of salt resulted by partial evaporation was 53.02% Ca, 28.93% O, 9.50% Na, 2.10% Mg, 1.53% Sr, 1.20% Cl, 1.10% Si, 0.63% K, 0.40% S, 0.39% Al. The salt resulted by total evaporation was indicated namely as NaCl. Whereas salt resulted by partial evaporation was CaCO₃ with a purity of 90% from High Score Plus analysis. In the experiment by chemical precipitation was reported that the reagents of ammonium carbonate were more reactive for synthesizing calcium salt from brine water compared to reagents of oxalate acid and ammonium hydroxide. The salts precipitated by NH₄OH, (NH₄)₂CO₃, and H₂C₂O₄ reagents were indicated as NaCl, CaCO₃ and CaC₂O₄.H₂O, respectively. The techniques of partial evaporation until 20% volume sample of brine water and chemical precipitation using (NH₄)₂CO₃ reagent are recommended in the synthesis of calcium salts from brine water because are simple, flexible and economical.

1. Introduction

Calcium is a mineral that is essential for life, good for living beings as well as for the needs of the industry, agriculture, pharmaceuticals and other chemicals. Calcium is an important determinant of water harness, and it also functions as a pH stabilizer, because of its buffering qualities. Calcium also gives water a better taste. Calcium salts that are often encountered in daily life are calcium carbonate. It is an ingredient utilized as filler in paper, paint, sealants and coatings [1][2]. It also has many applications in agriculture and the food industry [3][4]. Some agricultural uses of this substance are as animal feed and agricultural lime for soil. Many foods and cooking products, such as baking powder, dough and dry mixes also contain calcium carbonate. It is also an ingredient in toothpaste.

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Many natural resources in Indonesia, which can be used as a source to obtain calcium salts is sea water, brine water, limestone. Nowadays, calcium salts are abundantly synthesized from limestone and sea water compared to brine water resources. It becomes an interesting potential if could take advantage of brine water as raw material for the manufacture of the calcium salt. Brine water is a solution that has a high salt concentration. It comes from byproduct of reducing salt content process in seawater (desalination) so that brine water containing some of dissolved salts [5].

Few researchers have done experiments for synthesizing calcium salt from natural resources as follows: Wenhao Sun et al. [6] tried to know mechanisms of nucleation of metastable aragonite $\text{CaCO}_3$ in seawater. He observed that there are a direct relationship between the calcite surface energy and solution $\text{Mg}^{2+}$-$\text{Ca}$ ion concentrations. It showed the calcite nucleation barrier surpasses that of metastable aragonite in solutions with $\text{Mg}^{2+}$-$\text{Ca}$ ratios consistent in seawater, allowing aragonite to dominate the kinetics of nucleation. Ljerka Brecevic and Damir Kralj [7] said that calcium carbonates can be precipitated in the form of six modifications (polymorphic or hydrated). They consisted of crystal growth and transformation of amorphous calcium carbonate, calcium carbonate hexahydrate, calcium carbonate monohydrate, vaterite and calcite. Keith E. Chase and Erwin [8] Suess explained the addition of $\text{Ca}^{2+}$ or $\text{CO}_3^{2-}$ ions could increase supersaturation from seawater that would begin rapid precipitation of $\text{CaCO}_3$. Ritika Gupta [9] tried to synthesize of precipitated calcium carbonate nanoparticles using modified emulsion membranes. She has successful prepared calcium carbonate nanoparticles with particle size ranging from 100 nm to 1200 nm.

On this opportunity, we would investigate the effects of partial evaporation and chemical reagents in the synthesis of calcium salt from brine water resources in Indonesia. The chemical reagents used in the study was oxalate acid ($\text{C}_2\text{H}_2\text{O}_4$), ammonium carbonate ($\left(\text{NH}_4\right)_2\text{CO}_3$) and ammonium hydroxide ($\text{NH}_4\text{OH}$) that was the type of acidic, neutral, alkaline reagents. From this research could be obtained the following data such as cheaper technology and an effective reagent in extracting calcium from brine water to form calcium salts.

2. Experimental

The sample was originally from brain water, Tirta Sanita, Bogor. Whereas the chemical reagent used in the research were purchased from Merck with analytical pure grade that was oxalate acid ($\text{C}_2\text{H}_2\text{O}_4$), ammonium carbonate ($\left(\text{NH}_4\right)_2\text{CO}_3$) and ammonium hydroxide ($\text{NH}_4\text{OH}$).

![Figure 1. Brine water sample](image)

For identifying chemical composition of brine water was carried out total evaporation processes on sample, than the resulted residue was characterized by X-Ray Florescence (XRF) and X-ray Diffraction (XRD) analysis as shown in Table 1 and Fig. 2.

| Element | Ca | O | Na | Mg | Sr | Cl | Si | K | S | Al |
|---------|----|---|----|----|----|----|----|---|---|----|
| Mass (%)| 2.94 | 22.33 | 28.87 | 9.17 | 0.71 | 30.02 | 1.51 | 1.23 | 0.55 | 1.31 |

In this experiment, the formation mechanism of calcium salt was investigated. The processing methods were partial evaporation and chemical precipitation. The procedure was 10 liters of brine water evaporated until 20% volume sample and continued with filtration process to separate brine...
water filtrate from residue product. Residue resulted from evaporation process was characterized by X-ray Fluorescence (XRF) to identify chemical element of residue. Scanning electron microscopy/energy (SEM) to know morphology particle and X-ray diffraction (XRD) to identify phase of residue product. Filtrate of brine water then was reacted with C$_2$H$_2$O$_4$, (NH$_4$)$_2$CO$_3$ and NH$_4$OH reagents to get salt products in atmospheric condition and variation ratio volume brine water/chemicals (v/v) as follows: [10/1; 10/5; 10/10; 10/20; 10/30; 10:50; 20/1; 20/5; 20/10; 20/20; 20/30; 20:50]. The salt product than were filtered, dried, measured weights and finally characterized by SEM/EDS and X-ray diffraction (XRD) to identify phase of salt products. The flowchart of research is shown in Fig. 3.

**Figure 2.** The XRD pattern of brine water after total evaporation process

**Figure 3.** The flowchart of research
3. Result and Discussion

The brine water from Tirta Sanita, Bogor has murky green colorless and smelled like sulfur as shown in Fig. 1. From XRF analysis in Table 1 shows the chemical composition of brine water is 28.87% Na, 9.17% Mg, 2.94% Ca, 22.33% O, 0.71% Sr, 1.51% Si, 1.23% K, 0.55% S, 1.31% Al. It describes the resources of brine water consisted of sodium, calcium, magnesium and chloride elements that have the percentage higher than other elements. If brine water was carried out total evaporation process, it would form precipitated salts as shown in Fig. 2. Figure 2 looks that the peaks of diffraction are clearly and sharply at 2\(\theta\) degree of 27.44\(^{\circ}\); 31.79\(^{\circ}\); 45.58\(^{\circ}\); 54.02\(^{\circ}\); 56.63\(^{\circ}\); 66.42\(^{\circ}\). Based on PDF No. 04-002-2489, It is indicated namely as sodium chloride (NaCl). This is suitable with the data of chemical composition in Table 1 that the sodium (Na) and chloride (Cl) elements has the highest percentage compared to other elements. Therefore the phase of NaCl appears more dominant than other phases.

The diffraction peaks of other salts have not looked clearly in Fig. 2 because has lower intensity than the diffraction peaks of NaCl salt. It would become economical if brine water could be utilized for synthesizing calcium salts. We know that the consumption of calcium salt is predicted a rise slightly every year in the world. The formation mechanism of calcium salts of brine water would be explained in this research.

3.1. The effect of partial evaporation on the chemical composition, morphology and phase of residue product

In this research would be investigated the effect of partial evaporation on the chemical composition, morphology and phase of residue product. For describing and comparing the chemical composition and morphology of residue product resulted from total evaporation and partial evaporation until 20% volume sample of brine water was carried out the SEM and XRF analysis as represented in Table 2 and Fig. 4.

| Element            | Ca  | O    | Na  | Mg  | Sr  | Cl  | Si  | K   | S   | Al  |
|--------------------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Brine water (%)    | 2.94| 22.33| 28.87| 9.17| 0.71| 30.02| 1.51| 1.23| 0.55| 1.31|
| Residue from partial evaporation (%) | 53.02 | 28.93 | 9.50 | 2.10 | 1.53 | 1.20 | 1.10 | 0.63 | 0.40 | 0.39 |

From Table 2 looks that the chemical composition of residue product by partial evaporation is 53.02% Ca, 28.93% O, 9.50% Na, 2.10% Mg, 1.53% Sr, 1.20% Cl, 1.10% Si, 0.63% K, 0.40% S, 0.39% Al. It appears the percentage of calcium element increased from 2.94% to 53.02% by partial evaporation until 20% volume sample of brine. Partial evaporation undertaken is able to increase supersaturation of brine water so that precipitation of calcium element could occur rapidly in hours. Based on Table 2 could be explained that calcium element is easier precipitated than sodium and magnesium elements by partial evaporation techniques.

![Figure 4](image-url)
Fig. 4 describes the morphology of residue products by total evaporation and partial evaporation. It represents particles has irregular morphology like cubic for residue product by total evaporation and almost regular morphology like spherical for residue product by partial evaporation. On observation by SEM with magnification at 100 x also looks the particle sizes of residue product by total evaporation is approximately 100 μm that were larger than particles sizes by partial evaporation. It probably caused agglomeration of particles from brine water such as salts elements (Na, Ca, Mg, K) so that appears larger and irregular by SEM observation. The growth of NaCl crystal is more dominant than other salt crystals by total evaporation. Kazunori Kadota et al. [10] reported the precipitated NaCl and KCl particles have asymmetric structure. He also explained that other surfaces in contact with the aqueous phase were a flat cubic structure.

This condition is different with residue product by partial evaporation that has smaller particle size with regular particle distribution. It is probably indicated that particles resulted by partial evaporation is dominant as calcium elements with homogeneous particles. The difference of morphology of particles depends on evaporation condition. Takiyama et al. [11] concluded that the shape of the crystals was found to differ with the operating conditions. For identifying the phase of residue product by partial evaporation was carried out the XRD analysis as represented in Fig. 5.

![Figure 5. The XRD pattern of residue product on variation evaporation techniques: (a) total evaporation; (b) partial evaporation](image)

Fig. 5 looks that the phase of residue product changes with different evaporation techniques. At explaining above, it is known that the phase of residue product by total evaporation is sodium chloride (Fig. 2 or Fig. 5a). Whereas the result of XRD analysis from residue product by partial evaporation (Fig. 5b) shows the peaks of diffraction is clearly and sharply at 2θ degree of 23.3°; 29.67°; 36.3°; 39.8°; 43.54°; 47.87°; 48.91°; 57.91°; 61.3°. It is known namely as calcium carbonate (CaCO3) that is approximately 90 % CaCO3 from High Score Plus analysis.

The mechanism of CaCO3 formation based on chemical thermodynamics that the precipitation of solid phase (CaCO3) is controlled by the law of mass action. The purpose of partial evaporation is to create a solution of brine water become supersaturation condition with ion activation product (IAP) > solubility product (Ksp). For this condition, IAP = [Ca²⁺][CO₃²⁻] and Ksp (CaCO3) = 10⁻⁸.₄₈ (Table 3). Therefore [Ca²⁺][CO₃²⁻] > 10⁻⁸.₄₈, it causes precipitation of CaCO3 in brine water. This research is such interesting because calcium element was precipitated firstly besides other elements. It could be looked from the Data of Ksp as shown in Table 3. If the value of Ksp is low, it would rapid precipitation of solid phase.
Table 3. The solubility product (Ksp) of brine salt product

| Compound               | pKsp | Ksp        | Classification rule | Ref |
|------------------------|------|------------|---------------------|-----|
| CaCO₃                  | 8.48 | 10⁻⁸.⁴⁸    | insoluble           | [12]|
| CaC₂O₄                 | 2.27 | 10⁻².⁷⁷    | insoluble           | [13]|
| Na₂CO₃, 10H₂O          | 1.31 | 10⁻¹.⁴ⁱ    | insoluble           | [12]|
| Na₂C₂O₄                | -3.26| 10⁻².⁲⁶    | Soluble             | [13]|
| MgCO₃                  | 8.03 | 10⁻⁸.⁰³    | insoluble           | [12]|
| MgC₂O₄                 | -    | -          | -                   | [13]|
| CaCl₂, 6H₂O            | -4.09| 10⁺⁻⁴.⁰⁹   | Soluble             |     |
| NaCl                   | -1.58| 10⁻¹.⁵⁸    | Soluble             | [12]|
| MgCl₂, 6H₂O            | -4.39| 10⁻¹.⁴⁹    | Soluble             |     |
| KCl                    | -0.85| 10⁻¹.⁸³    | Soluble             |     |

Table 3 shows that CaCO₃ salt has Ksp value lower than other salts such as CaC₂O₄, Na₂CO₃, 10H₂O, MgCO₃ (insoluble). Therefore the CaCO₃ salt would begin to form a precipitation more rapid than other salts in supersaturation condition of brine water.

3.2. The effect of chemical precipitation processes on the morphology and phase of salt product

In this research, the synthesis of calcium salt was conducted by chemical precipitation techniques using several reagents, such as oxalic acid (H₂C₂O₄), ammonium carbonate ((NH₄)₂CO₃) and ammonium hydroxide (NH₄OH), which each reagent would react with elements in the filtrate of brine water to form complex precipitates. The influence of reagent and ratio volume (v/v) the concentrated brine water (filtrate)/reagents would form precipitates differently. Formation of the precipitated product such as calcium salt would be explained detail in this research to indicate the kind of reagent and ratio volume (v/v) concentrated brine water/reagents that are optimum for synthesizing calcium salt. The precipitated products resulted by chemical precipitation are presented in Table 4.

Table 4. The formation of salt from the concentrated brine water in variation ratio volume (v/v) concentrated brine water (filtrate)/reagents and variation reagents

| Ratio Reagents | 10:1 | 10:5 | 10:10 | 10:20 | 10:30 | 10:40 | 10:50 |
|----------------|------|------|-------|-------|-------|-------|-------|
| Salts using H₂C₂O₄ (gram) | 4.28 | 4.4 | 4.7 | 4.68 | 4.78 | 4.8 | 4.72 |
| Salt using (NH₄)₂CO₃ (gram) | 4.08 | 4.2 | 4.25 | 4.2 | 4.25 | 4.2 | 4.25 |
| Salt using NH₄OH (gram) | - | 3.62 | 3.70 | 3.87 | 4.05 | 3.78 | 3.84 |

| Ratio Reagents | 20:1 | 20:5 | 20:10 | 20:20 | 20:30 | 20:40 | 20:50 |
|----------------|------|------|-------|-------|-------|-------|-------|
| Salts using H₂C₂O₄ (gram) | 4.31 | 5.21 | 5.39 | 5.2 | 5.4 | 5.4 | 5.8 |
| Salt using (NH₄)₂CO₃ (gram) | 4.29 | 4.73 | 4.89 | 5.12 | 4.48 | 4.31 | 4.38 |
| Salt using NH₄OH (gram) | - | 4.18 | 4.19 | 4.17 | 4.2 | 3.96 | 3.65 |

According to Table 4 looks that by using both oxalic acid and ammonium carbonate reagents, it would form precipitated salts more rapid (faster) than by using ammonium hydroxide at ratio volume (v/v) concentrated brine water/reagents of 10:1 and 20:1. It could be seen in the formation of brine salt using ammonium hydroxide reagent at ratio of 10:1 and 20:1 that did not produce precipitates. The
brine salt by using ammonium hydroxide begins to form at a ratio of 10:5 and 20:5. The formation of precipitated brine salt is maximum at ratio volume (v/v) concentrated brine water/reagents of 10:10 and 20:20 using ammonium carbonate; 10:30 and 20:50 using oxalate acid; 10:30 using ammonium hydroxide. From this research could be concluded briefly that the number of reagents of ammonium carbonate used to form a precipitate is less than reagents of oxalate acid and ammonium hydroxide. It shows that the reagent of ammonium carbonate is more reactive for synthesizing calcium salt from brine salt compared to reagents of oxalate acid and ammonium hydroxide. It is also supported with the data of Ksp of salt carbonate (CaCO₃) that shows lower than the data of Ksp of other salts in Table 3. Keith E et al. [8] reported addition of CO₃²⁻ ion to seawater would increase supersaturation and finally would begin rapid CaCO₃ precipitation.

To determine the morphology and chemical composition of salt brine was carried out by SEM-EDS analysis. The SEM-EDS analysis is not representative, because the results are based on only one point or area from a sample shot X-ray. This analysis aimed to compare the morphology and the chemical composition of salt brine with semi quantitative through chemical precipitation techniques. The morphology and chemical composition of salt brine is shown in Fig. 6 and Table 5

**Figure 6.** The morphology of brine salt by chemical precipitation using: (a) Oxalate acid; (b) Ammonium carbonate; (c) Ammonium hydroxide

The results of SEM analysis shows the morphology of salt brine precipitate is different that depend on a kind of reagents. In the salt brine formed using a reagent oxalic acid will produce irregular morphology like cubic. On the SEM results of precipitate with ammonium carbonate reagent has spherical shape morphology, while the SEM results of precipitate with ammonium hydroxide reagent has a larger size at the same magnification 1000x compared with both other precipitates.

### Table 5. The semi quantitative of chemical composition from salt brine by EDS-SEM

| Element | Oxalate salt | Carbonate Salt | Hydroxide Salt |
|---------|--------------|----------------|---------------|
| Ca      | 17.64 %      | 39.91 %        | 3.47 %        |
| K       | 0.02 %       | 0.41 %         | 0.91 %        |
| Cl      | 0.26 %       | 0.17 %         | 24.28 %       |
| Al      | 0.10 %       | 0.05 %         | 0.78 %        |
| Mg      | 1.52 %       | 2.15 %         | 16.91 %       |
| Na      | 15.22 %      | 0.98 %         | 9.95 %        |
| O       | 43.85 %      | 46.82 %        | 29.25 %       |

Table 5 shows the chemical composition of salt precipitated by oxalate acid, ammonium carbonate and ammonium hydroxide reagents. It looks that the brine salt precipitated by oxalate acid and ammonium carbonate reagents has the calcium percentage higher than by ammonium hydroxide reagent. The salt precipitated by oxalate acid consists of calcium and sodium elements with high levels
that were spread evenly in salt. It causes the morphology of salt precipitated by oxalate acid is irregular spherical (Fig. 6a). The same thing is also shown on the salt precipitated by ammonium hydroxide that salt consisted of sodium, magnesium, chloride with high levels besides other elements. On the precipitation using ammonium hydroxide, there are agglomerations of elements from brine water when begin the crystal growth together. It causes the morphology of particles appeared irregular and larger (Fig. 6c)[10][11].

From EDS-SEM analysis in Table 5 could be seen that salt precipitated by ammonium carbonate has chemical composition as follows: 39.91% Ca, 0.41% K, 0.17% Cl, 0.05% Al, 2.15% Mg, 0.98% Na, 46.82% O. It shows that the calcium element is the most dominant precipitated by ammonium carbonate. Therefore the morphology of salt precipitated by (NH$_4$)$_2$CO$_3$ reagent has spherical shape and appeared more regular. For identifying the phase of brine salts precipitated by H$_2$C$_2$O$_4$, (NH$_4$)$_2$CO$_3$, NH$_4$OH reagents were carried out the XRD analysis as shown in Fig. 7.

![Figure 7](image)

**Figure 7.** The XRD pattern of salts resulted by chemical precipitation using variation reagents: (a) ammonium hydroxide; (b) ammonium carbonate; (c) oxalate acid

The peaks of diffraction are clearly and sharply at 2θ degree of 27.44°; 31.79°; 45.58°; 54.02°; 56.63°; 66.42° as represented in Fig. 7. Based on PDF No. 04-002-2489, it is indicated namely as sodium chloride (NaCl). This is supported with the data of chemical composition in Table 1 that the Na, Mg and Cl elements have higher percentage than other elements for chemical precipitation using NH$_4$OH. On this condition, salt of NaCl is precipitated earlier than MgCl$_2$ because value Ksp of NaCl is smaller than Ksp of MgCl$_2$ as shown Table 3. Therefore salt precipitated by NH$_4$OH is indicated as NaCl. From this research could be explained that the NH$_4$OH reagent is not suitable used for synthesizing calcium salt from brine water.

Fig. 7b shows that the peaks of diffraction from salt precipitated by (NH$_4$)$_2$CO$_3$ are clearly and sharply at 20 degree of 23.3°; 29.67°; 36.3°; 39.8°; 43.54°; 47.87°; 48.91°; 57.9°; 61.3°. It is known as calcium carbonate (CaCO$_3$). The Ca$^{2+}$ ion of brine water is almost precipitated completely using (NH$_4$)$_2$CO$_3$ reagents[8]. This technique of chemical precipitation using (NH$_4$)$_2$CO$_3$ is recommended for synthesizing calcium salt from brine water.

On observation in Fig. 7c looks that the peaks of diffraction from salt precipitated by H$_2$C$_2$O$_4$ are clearly and sharply at 20 degree of 14.89°; 24.36°; 30.02°; 38.14°; 43.17°; 46.41°. It is indicated as calcium oxalate (CaC$_2$O$_4$.H$_2$O). The chemical precipitation using H$_2$C$_2$O$_4$ reagent is also recommended for synthesizing calcium salt from brine water. However the rate of CaCO$_3$ precipitation is faster than CaC$_2$O$_4$.H$_2$O precipitation.
4. Conclusion
The result of experiment showed that the chemical composition of brine water from Tirta Sanita, Bogor was 28.87% Na, 9.17% Mg, 22.33% Ca, 30.02% O, 0.71% Sr, 1.51% Si, 1.23% K, 0.55% S, 1.31%. The salt precipitated by total evaporation was indicated namely as sodium chloride (NaCl). The chemical composition of salt resulted by partial evaporation was 53.02% Ca, 28.93% O, 9.50% Na, 2.10% Mg, 1.53% Sr, 1.20% Cl, 1.10% Si, 0.63% K, 0.40% S, 0.39% Al. It was known namely as calcium carbonate (CaCO₃) with a purity of 90% CaCO₃ from High Score Plus analysis. The particles have irregular morphology like cubic for salt resulted by total evaporation and regular (homogenous) morphology like spherical for salt resulted by partial evaporation. For the synthesis of calcium salt by chemical precipitation was obtained information as follows: the reagents of ammonium carbonate were more reactive for synthesizing calcium salt from brine water compared to reagents of oxalate acid and ammonium hydroxide. The salts precipitated by NH₄OH, (NH₄)₂CO₃ and H₂C₂O₄ reagents are indicated as NaCl, CaCO₃ and CaC₂O₄·H₂O, respectively. The morphology of salt resulted by chemical precipitation was irregular with asymmetric structure using NH₄OH reagent, spherical shape with homogeneous particles using (NH₄)₂CO₃ reagent, and irregular spherical morphology using H₂C₂O₄ reagent. From this research could be concluded briefly that the technique of partial evaporation until 20% volume sample of brine water and chemical precipitation using (NH₄)₂CO₃ reagent are recommended in the synthesis of calcium salts from brine water for domestic and industry applications. These technologies are simple, flexible and economical.

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