Preparation and Characterization of Sorbent for Phosphate Removal from Hydrated Lime and Blast Furnace Slag

Guozhuo Gong\textsuperscript{1,2}, Shufeng Ye\textsuperscript{1}, Qi Wang\textsuperscript{3}
Lianqi Wei\textsuperscript{1,2}, Jiandi Ni\textsuperscript{1,2} and Yunfa Chen\textsuperscript{1}

1. State Key Laboratory of Multi-phase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100080, China.
2. Graduate University of Chinese Academy of Sciences, Beijing, 100049, China.
3. School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China.

Abstract: The adsorption of dissolved inorganic phosphate on sorbents produced by hydrated lime and blast furnace slag was fundamentally studied basing on an orthogonal experiment design. The sorbents prepared were characterized, the adsorption tests were carried out, and the effects of preparation variables and the reaction between hydrated lime and blast furnace slag on their phosphorus (P) adsorption were evaluated. Furthermore, some of sorbents were selected to do equilibrium and kinetic studies.

It is found that sorbents prepared are materials with porosity in the mesopore range, and the specific surface area of sorbents prepared is larger than that of hydrated lime or blast furnace slag alone due to the formation of calcium silicate hydrates, which are mainly C-S-H(I).

To clarify the role of pozzolanic reactions on the P adsorption, the increment of P adsorption capacity for sorbent is obtained by eliminating the effect of raw materials. It is found that all sorbents prepared show lower P adsorption capacity than Ca(OH)\textsubscript{2}, but much higher than blast furnace slag. The weight ratio of blast furnace slag/hydrated lime is the most important preparation variable for P adsorption capacity and its increment, and with the increase of weight ratio of blast furnace slag, P adsorption capacity of sorbent decreases, but its increment increases. When the weight ratio of blast furnace slag/hydrated lime is equal or less than 3/7, the increment of P adsorption capacity is independent of the specific surface area of sorbent, but when the weight ratio of blast furnace slag/hydrated lime is more than 3/7, the increment is seen to increase linearly from 29.15mg g\textsuperscript{-1} to 57.91mg g\textsuperscript{-1} as the specific surface area increases from 27.00 m\textsuperscript{2} g\textsuperscript{-1} to 62.39 m\textsuperscript{2} g\textsuperscript{-1}.

For the sorbents prepared in the experiment, the Langmuir model has a better correlation with the experimental data than the Freundlich model, and the adsorption of P can be described by the pseudo second-order equation.

Keywords: Phosphate removal; Blast furnace slag; Hydrated lime.

1. INTRODUCTION

Phosphorus (P) is used in many consumer products and industrial processes that involve particles of a colloidal nature. Examples of such applications are as diverse as fertilizers, detergents, pigment formulation, water treatment and mineral processing. P discharged into the surface waters stimulates the growth of aquatic micro- and macro-organisms in nuisance quantities, which in excess can cause eutrophication in stagnant water bodies.\cite{1-5} Therefore, removal of P from the wastewaters can be an effective method for the control of eutrophication in lakes and similar stagnant water bodies.\cite{6,7}

Many methods have been developed to remove excessive phosphate from water.\cite{8-22} The biological method is low-cost but the variability in chemical composition and temperature of wastewater would make the implementation of this process not feasible for wastewater treatment. Other P removal techniques are chemical treatments like adsorption, chemical precipitation, ion exchange and electrodialysis. Adsorption and chemical precipitation among the above methods have been widely used for phosphate removal. P removal through sorbents,\cite{6} such as activated alumina, fly ash, zeolite, different soils including metal oxides, goethite, pumice, titanium dioxide have been investigated.

Blast furnace slag (BFS) \cite{1,3-5,11,14,16,19,22} is an alternative and favorable sorbent for phosphate because it contains large amounts of calcium. However, the application of slags in the adsorption of P from aqueous solutions faces a number of problems, too. BFS is a complex CaO-MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} system which also incorporates a number of minor components that can concentrate on the slag surface during crystallization or during transition to the glassy state, and can affect the adsorption of phosphates. The reaction of these oxides with water may be alkaline (CaO), acidic (SiO\textsubscript{2}) or amphoteric (MgO, Al\textsubscript{2}O\textsubscript{3}), and the hydration equilibrium may take several days to establish.\cite{4}

In this article, hydrated lime (HL) was used as activator to destroy the surface of BFS to try to increase the P admassorption capacity of BFS. A series of sorbents for phosphate removal were prepared from hydrated lime and blast furnace slag basing on an orthogonal experiment design. The sorbents prepared were dried and characterized by SEM and XRD analysis, and the porosities of the resultant sorbents were characterized by nitrogen adsorp-
2. EXPERIMENTAL SECTION

2.1. Sorbents preparation and designs of experiment

Sorbents were prepared using commercial Ca(OH)$_2$ supplied by Beijing Chemical Reagents Company and BFS supplied by Jinan Iron and Steel Company Limited. The chemical composition and physical properties of these materials is shown in Table 1.

A full factorial design was used to synthesize sorbents by varying four experimental variables: the hydration time (t$_s$), the weight ratio of blast furnace slag/hydrated lime (BFS/HL), the slurring temperature (T) and the ratio of water/solid (W/S). The solid materials were kept at a constant value of 15g. Table 2 displays the matrix for the 4$^4$ factorial design. The procedure used to prepare the sorbents comprised the following steps: BFS/HL slurries were added by the required ratio in a 250 ml polypropylene conical beaker which was heated by a hot plate equipped with a magnetic stirrer which was kept at a rate of 700 rpm. The mouth of the beaker was plugged to prevent water loss and the interference of CO$_2$. After slurring the sample was placed into a vacuum oven at 35$^\circ$C for about 24h to evaporate most of the free water and then further heated to 100$^\circ$C to dry, which was in about 2-4 days. The dried sorbents were then pelletized, crushed and sieved to produce the required particle size range (60-20 $\mu$m).

2.2. Adsorption experiment

Adsorption studies were carried out by shaking conical flasks with different concentration of KH$_2$PO$_4$ (as P) solution and 0.2 g of sorbent in the bottles for 6 h at 30$^\circ$C. After equilibrium, the samples were filtrated by filter paper and clear filtrates were taken and analyzed for phosphate spectrophotometrically. The amount of phosphate adsorbed per unit of sorbents was calculated by:

\[
q = \frac{C_0 - C_f}{m} V
\]
Preparation and Characterization of Sorbent for Phosphate Removal from Hydrated Lime and Blast Furnace Slag

Corresponding author: S. F. Ye, sfye@home.ipe.ac.cn

\[
q = \frac{(c_i - c_e)V}{m}
\]  (1)

where \(q\) (mg g\(^{-1}\)) is the amount of the phosphate adsorbed per unit mass of sorbent (adsorption capacity), \(c_i\) (mg L\(^{-1}\)) and \(c_e\) (mg L\(^{-1}\)) are the initial and final concentrations of the phosphate in solution, respectively. \(V\) (L) is the solution volume, and \(m\) is the mass of sorbent.

Adsorption kinetics was carried out using 100 ml of KH\(_2\)PO\(_4\) solution containing the desired concentration and 0.2 g of sorbent in 250 ml conical flasks shaking by water shaker. At predetermined time intervals, samples were separated by filter paper and analyzed by spectrophotometer. Adsorption isotherms’ method was very similar with adsorption kinetics, the difference was that adsorption isotherms were carried out with different initial KH\(_2\)PO\(_4\) concentration and fixed adsorption time for 6 h.

2.3. Characterization of sorbents

SEM photographs of the sorbents were taken in a JEOL JSM-6700F system, in order to observe the macrostructural change due to hydration reaction. XRD patterns were recorded on a Panalytical X’Pert PRO system for the powdered samples less than 100 µm, with Cu-K\(_\alpha\) radiation at a sweep rate of 3° min\(^{-1}\). The specific surface area of sorbents were determined using the BET methods on an Autosorb 1C Quantachrome analyzer.

Fig. 1. \(\text{N}_2\) adsorption/desorption isotherm of S2

3. RESULTS AND DISCUSSION

3.1. Characterization of sorbents

Fig. 1 is the \(\text{N}_2\) adsorption/desorption isotherm of S2. When subjected to \(\text{N}_2\) gas desorption, the isotherm reveals a hysteretic behaviour for the sorbent. The hysteresis observed at higher relative pressures (>0.5) suggests that it is material with porosity in the mesopore range. This result can be obtained by other sorbents prepared. Table 2 summarizes the specific surface areas of sorbents prepared by various conditions and raw materials of Ca(OH)\(_2\) and blast furnace slag. Nearly all of the BFS/HL sorbents have larger surface areas than the raw materials of Ca(OH)\(_2\) and blast furnace slag due to pozzolanic reactions.[23]

In general, pozzolanic reactions start with the chemical adsorption of calcium hydroxide on the surface of silanol groups.[24] Since the pH of the solution is high, SiO\(_2\) is dissolved, reacting with Ca(OH)\(_2\) to form calcium silicate(CSHs) which has large surface area and porous structure on the surface of SiO\(_2\) as follows:

\[
\text{SiO}_2(s) + x\text{Ca}_q + 2x\text{OH}_q + (y-x)\text{H}_2\text{O} \rightarrow x\text{CaO\cdot SiO}_2 \cdot y\text{H}_2\text{O} \tag{2}
\]

where \(x\) is 0.8~1.5, and \(y\) is 0.5~2.5.[25]

Scanning electron micrographs (SEMs) of the blast furnace slag and sorbent S16 are shown in Fig. 2. Fig. 2(a) shows the typical view of a BFS particle discharged from a steel factory. Coarse surface and irregular shape of the particle is readily apparent. Fig. 2(b) shows the typical view of sorbent S16. The surface of the BFS particle is destroyed, more surface of BFS particle emerges and some “foil-like” material covers on the surface of the slag particle, which can be found in other sorbents prepared.

The X-ray diffraction patterns of the BFS and sorbents S16 are shown in Fig. 3. Obviously, the irregular diffraction pattern of the BFS means it is amorphous. The X-ray diffraction pattern of sorbents S16 shows the existence of Ca(OH)\(_2\) and CSHs which can be seen in other sorbents. Compared to Ca(OH)\(_2\), the peaks of calcium silicate(CSHs) are weaker and belong to illcrystallized hydrated calcium silicate(CSHs) with 2θ at 29.8°, 32°, and 49.8°. Illcrystallized tobermorite includes C-S-H\[\text{Ⅰ}\], C-S-H\[\text{Ⅱ}\], and tobermorite gel.[26] Under the present experimental conditions, they are mainly C-S-H\[\text{Ⅱ}\], which is as same as the type of CSHs formed in the Ca(OH)\(_2\)/silica sorbents prepared by other researchers.[27,28]
3.2. Effect of preparation variables on the P adsorption

The results of capacity of P adsorption for the sorbents prepared by various conditions and raw materials of Ca(OH)\(_2\) and BFS are listed in Table 2. The results, in Table 2, show that all sorbents prepared show lower P adsorption capacity than Ca(OH)\(_2\), but much higher than BFS.

Table 3. Results of the ANOVA test for P adsorption capacity of BFS/HL sorbents.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Sum of squares</th>
<th>d.f.</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>p(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ts</td>
<td>98.81</td>
<td>3</td>
<td>32.94</td>
<td>3.02</td>
<td>0.194</td>
</tr>
<tr>
<td>W/S</td>
<td>96.50</td>
<td>3</td>
<td>32.17</td>
<td>2.95</td>
<td>0.199</td>
</tr>
<tr>
<td>BFS/HL</td>
<td>28739.98</td>
<td>3</td>
<td>9579.99</td>
<td>878.09</td>
<td>6E-05</td>
</tr>
<tr>
<td>T</td>
<td>45.29</td>
<td>3</td>
<td>15.10</td>
<td>1.38</td>
<td>0.398</td>
</tr>
<tr>
<td>Total error</td>
<td>32.73</td>
<td>3</td>
<td>10.91</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) d.f.: degrees of freedom. \(^{b}\) p: probability for F-ratio test.

Table 4. Results of the ANOVA test for \(\Delta s\) of sorbents.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Sum of squares</th>
<th>d.f.</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>p(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ts</td>
<td>92.52</td>
<td>3</td>
<td>30.84</td>
<td>2.48</td>
<td>0.24</td>
</tr>
<tr>
<td>W/S</td>
<td>100.78</td>
<td>3</td>
<td>33.59</td>
<td>2.70</td>
<td>0.22</td>
</tr>
<tr>
<td>BFS/HL</td>
<td>7114.40</td>
<td>3</td>
<td>2371.47</td>
<td>190.94</td>
<td>6E-04</td>
</tr>
<tr>
<td>T</td>
<td>42.52</td>
<td>3</td>
<td>14.17</td>
<td>1.14</td>
<td>0.46</td>
</tr>
<tr>
<td>Total error</td>
<td>37.26</td>
<td>3</td>
<td>12.42</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) d.f.: degrees of freedom. \(^{b}\) p: probability for F-ratio test.

3.3. Effect of pozzolanic reactions on the P adsorption

To clarify the role of pozzolanic reactions on the P adsorption, the increment of P adsorption capacity for sorbent is obtained by eliminating the effect of raw materials:

\[
\Delta_i = q_s - W_{BFS} \cdot q_{BFS} - (1 - W_{BFS}) \cdot q_{HL}
\]

where \(\Delta_i\) is the increment of P adsorption capacity for sorbent, \(q_s\) is the P adsorption capacity for sorbent, \(W_{BFS}\) is the weight ratio of BFS in the preparation procedure of sorbent, \(q_{BFS}\) is the P adsorption capacity of BFS, and \(q_{HL}\) is the P adsorption capacity of Ca(OH)\(_2\). The results of \(\Delta_i\) are shown in Table 2. The data calculated have also been used to do the ANOVA analysis, and the results are shown in Table 4. The weight ratio of BFS/HL is the most important variable for \(\Delta_i\), and other preparation variables effect \(\Delta_i\) little.

The relationship of \(\Delta_i\) with the weight ratio of BFS is shown in Fig. 4. It can be found that with the increase of the weight ratio of BFS, \(\Delta_i\) increases rapidly, and when the weight ratio of BFS is 0.9, \(\Delta_i\) is the biggest.

Fig. 4 shows the relationship of P adsorption capacity and the increment as a function of the weight ratio of BFS for BFS/HL sorbents.

In Table 3, the weight ratio of BFS/HL has P-value less than 0.001, indicating that it is significantly different from zero at the 99.9% confidence level, and it is the most important variable for P adsorption. The hydration time (ts), the ratio of water/solid (W/S) and the slurring temperature (T) have P-values more than 0.1, indicating that they effect P adsorption little.

Fig. 4 shows the relationship of P adsorption capacity with the weight ratio of BFS. It can be found that with the decrease of the weight ratio of BFS, P adsorption capacity of sorbent increases rapidly. It can be well understood since the P capacity of Ca(OH)\(_2\) is high.

Fig. 5 shows the relationship of \(\Delta_i\), with the specific surface area of sorbents. From the figure, it can be concluded that there are two relationships between the specific surface area and \(\Delta_i\). When the weight ratio of BFS/HL is equal or less than 3/7, \(\Delta_i\) is independent of the specific surface area of sorbent, and the increment is closed to zero. It means that pozzolanic reaction affects...
little on P adsorption. In this range of the weight ratio of BFS/HL, the proportion of Ca(OH)₂ in the sorbent is large, and the pore in the sorbent was blocked by the large amount of product of Ca₃PO₄ during the reaction process. So the specific surface areas and porosity structure in the sorbent did not play the role. In this condition, chemical precipitation may be the main reason for P adsorption. But when the weight ratio of BFS/HL is more than 3/7, \( \Delta_s \) is seen to increase linearly from 29.15mg g⁻¹ to 57.91mg g⁻¹ as the specific surface area increases from 27.00 m² g⁻¹ to 62.39 m² g⁻¹. In this case, both adsorption and chemical precipitation are the reasons for P adsorption. Within this specific surface area range, the linear trend can be described quantitatively by the following empirical equation with a correlation coefficient of 0.9526:

\[
\Delta_s = 0.7688S + 8.2488 \tag{4}
\]

where \( S \) is the specific surface area of sorbent.

Since the sorbents prepared is cataloged to two groups, we select one from each group to do equilibrium and kinetic studies.

### 3.4. Equilibrium studies

Adsorption isotherms are important for the description of how molecules of adsorbate interact with sorbent surface. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption. Two well known isotherm equations, the Langmuir and Freundlich, have been applied for deeper interpretation of the adsorption data obtained. Fig. 6 shows the adsorption isotherms of BFS, S10 and S16. Compared to S16 and BFS, there is no direct relationship between equilibrium concentration and the amount of solute adsorbed in S10, which indicates that chemical precipitation may be the main reason for P adsorption of S10.

The Langmuir model is represented from the linear form represented by the equation[6]:

\[
c_e / q_e = 1/(q_mK_a) + c_e / q_m \tag{5}
\]

where \( q_e \) is the amount of solute adsorbed per gram of sorbent and \( c_e \) is the equilibrium concentration of solute in the bulk of the solution. The constants \( K_a \) and \( q_m \) relate to the ion-exchange capacity and energy of ion-exchange, respectively.

The Freundlich equation is given as linear form of the equation[6]:

\[
\log q_e = 1/n \log c_e + \log K_f \tag{6}
\]

where \( K_f \) and \( n \) are constants which relate to adsorption capacity and adsorption intensity of the sorbent.

The values of the parameters of the two models and the related correlation coefficients (\( R^2 \) values) are listed in Table 5. The results show that the Langmuir equation better fits the adsorption equilibrium data over the concentration range used in this investigation than the Freundlich equation does. The linearized Langmuir isotherm of P adsorption by BFS, S10 and S16 is shown in Fig. 7. The fact that the Langmuir isotherm fits the experimental data well may be due to the homogeneous distribution of active sites on the gel surface since the Langmuir equation assumes that the surface is homogeneous and that the active sites have equal affinities for the molecules of the adsorbate.

### Table 5 Langmuir and Freundlich isotherms parameters at 303K

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>( q_m )</th>
<th>( K_a )</th>
<th>( R^2 )</th>
<th>( K_f )</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S16</td>
<td>135.14</td>
<td>0.0031</td>
<td>0.9993</td>
<td>25.86</td>
<td>0.23</td>
<td>0.9055</td>
</tr>
<tr>
<td>S10</td>
<td>208.33</td>
<td>0.0024</td>
<td>0.9999</td>
<td>114.60</td>
<td>0.11</td>
<td>0.5207</td>
</tr>
<tr>
<td>BFS</td>
<td>86.96</td>
<td>0.0037</td>
<td>0.9886</td>
<td>5.893</td>
<td>0.40</td>
<td>0.9505</td>
</tr>
</tbody>
</table>

Corresponding author: S. F. Ye, sfye@home.ipe.ac.cn
3.5. Kinetic studies

In order to obtain kinetic data for phosphate adsorption on sorbent prepared, the variation in phosphate concentration with time was measured. The experimental results are presented in Fig. 8. It is found that the adsorption of P has an increasing trend with increasing of time, and sorbent S10 is much quicker than S16 and BFS to establish equilibrium, providing evidence that intraparticle diffusion is the controlling resistance rather than the external diffusion.

The pseudo-first order and pseudo-second order kinetic models were selected to test the ion-exchange dynamics in this work because of their good applicability in most cases in comparison with the first and second order models[9]:

\[
\log(q_e - q_t) = \log q_e - k_1 t \\
t / q_t = 1/(k_2 q_e^2) + (1/q_e) t
\]

where \( q_e \) (mg g\(^{-1}\)) is the amount of P adsorption capacity at the time \( t \) (min), and \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the rate constants of the first- and second-order kinetic equations. The slopes and intercepts of these curves are used to determine the pseudo-first-order and pseudo-second-order constants \( k_1 \) and \( k_2 \), and the equilibrium capacity \( q_e \). The calculated (cal) value of \( q_e \) (Table 6) from the pseudo-first-order kinetics model is dramatically lower than the experimental (exp) value. However, the pseudo-second-order kinetics model (Fig. 9, Table 6) provides a near-perfect match between the theoretical and experimental \( q_e \) values. As a result, the ion-exchange process appears to follow pseudo-second-order reaction kinetics. The pseudo-second-order kinetics model also described the data better than the first-order model.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>( q_e ) (exp) (mg g(^{-1}))</th>
<th>( q_e ) (cal) (mg g(^{-1}))</th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( R^2 )</th>
<th>( q_e ) (cal) (g mg(^{-1}) min(^{-1}))</th>
<th>( k_2 ) (g mg(^{-1}) min(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S16</td>
<td>128.16</td>
<td>18.59</td>
<td>0.0024</td>
<td>0.6302</td>
<td>128.21</td>
<td>0.0016</td>
<td>0.9994</td>
</tr>
<tr>
<td>S10</td>
<td>195.17</td>
<td>128.59</td>
<td>0.0447</td>
<td>0.9607</td>
<td>204.08</td>
<td>0.0016</td>
<td>0.9988</td>
</tr>
<tr>
<td>BFS</td>
<td>39.20</td>
<td>33.87</td>
<td>0.0051</td>
<td>0.9564</td>
<td>38.17</td>
<td>0.00043</td>
<td>0.9983</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

In this article, a series of sorbents for phosphate removal were prepared from hydrated lime and blast furnace slag basing on an orthogonal experiment design.

It is found that sorbents prepared were material with porosity in the mesopore range, and the specific surface area of sorbents prepared are larger than those of hydrated lime or blast furnace slag alone due to the formation of calcium silicate hydrates, which are mainly C-S-H(I). All sorbents prepared show lower P adsorption capacity than Ca(OH)\(_2\), but much higher than BFS.

To clarify the role of pozzolanic reactions on the P adsorption, the increment of P adsorption capacity for sorbent is obtained by eliminating the effect of raw materials. It is found that pozzolanic reaction can increase the P adsorption capacity of sorbents. The weight ratio of hydrated lime/blast furnace slag(9/1-1/9) is the most important preparation variable for P adsorption and its increment, and other variables such as hydration time(45min-17h), the slurring temperature(50\(^\circ\)-80\(^\circ\)) and the ratio of water/solid(10/1-25/1) effect P adsorption and its increment little. With the increase of weight ratio of BFS/HL is equal or less than 3/7, the increment of P adsorption capacity decreases, but its increment increases. When the weight ratio of BFS/HL is equal or less than 3/7, the increment of P adsorption capacity decreases, but its increment increases.

Corresponding author: S. F. Ye, sfye@home.ipe.ac.cn
adsorption capacity is independent of the specific surface area of sorbent, and the increment is zero. But when the weight ratio of BFS/HL is more than 3/7, the increment is seen to increase linearly from 29.15 mg g \(^{-1}\) to 57.91 mg g \(^{-1}\) as the specific surface area increases from 27.00 m\(^2\) g \(^{-1}\) to 62.39 m\(^2\) g \(^{-1}\).

In addition, the Freundlich and Langmuir models were used to simulate the adsorption equilibrium. The results indicate that for the sorbents prepared in the experiment, the Langmuir model has a better correlation with the experimental data than the Freundlich model. Pseudo first-order equation and pseudo second-order equation were selected to follow the adsorption process. It is shown that the adsorption of P can be described by the pseudo second-order equation.

REFERENCES

Corresponding author: S. F. Ye, sfye@home.ipe.ac.cn