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Hernández Hernández, Román Ángel; Legorreta García, Felipe; Hernández Cruz, Leticia Esperanza;
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Statistical Treatment of Bleaching Kaolin by Iron Removal

Román Ángel Hernández Hernández,*¹ Felipe Legorreta García,¹ Leticia Esperanza Hernández Cruz,¹ and Antonia Martínez Luévanos²

¹ Universidad Autónoma del Estado de Hidalgo. Área Académica de Ciencias de la Tierra y Materiales. Carretera Pachuca-Tulancingo, Km 4.5 s/n, Mineral de la Reforma, Hidalgo, México., C.P. 42184. angelitofox3@hotmail.com

² Universidad Autónoma de Coahuila, México. Blvd. V. Carranza y González Lobo s/n; Saltillo, Coahuila., México., C. P. 25280

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Abstract. In the present study, oxalic acid was used as a leaching reagent to remove iron from a kaolin mineral. Statistical analysis was conducted to determine the most influential factors in the dissolution of iron from the kaolin mineral. Our goal was ferric iron solubilization and its reduction to ferrous iron to improve the iron removal in the acid medium. Leaching experiments were conducted at atmospheric pressure. A two-level factorial design of the type 2⁴ was utilized. The dependent variable was the percentage of dissolved iron, and the dependent variables in this study were acid concentration (0.35 and 0.50 M), temperature (75 °C and 100 °C), leaching time (2 and 4 h), and pH (1.5 and 2.5). An analysis of variance revealed that the effects of the factors temperature (b), pH (d), and the combined effects of temperature and time (bc) resulted in the maximum dissolution of iron of 88% at 100 °C, giving a kaolin mineral with a whiteness index 93.50%.

Keywords: Kaolin mineral, dissolution of iron, oxalic acid, factorial design.

Resumen. Se presenta el tratamiento estadístico de la disolución de hierro de un mineral caolinitico utilizando soluciones de ácido oxálico como agente lixiviante. La base de este proceso es la solubilización de hierro férrico y su reducción a hierro ferroso para mejorar su remoción. Los experimentos de lixiviación a presión atmosférica se realizaron bajo un diseño estadístico factorial 2⁴. La variable de respuesta fue el porcentaje de hierro disuelto, los factores estudiados y que tuvieron un efecto importante en la lixiviación fueron: la concentración de ácido oxálico (0.35 y 0.50 M), la temperatura (75° C y 100 °C), el tiempo de lixiviación (2 y 4 horas) y el pH (1.5 y 2.5). El análisis de varianza indicó que los factores temperatura (b) y pH (d), así como la combinación temperatura-tiempo (bc) permitieron conseguir una máxima disolución de hierro de 88% a 100 °C obteniendo mineral caolinitico con un índice de blancura de 93.5 %.

Palabras clave: Mineral caolín, disolución de hierro, ácido oxálico, diseño factorial.

Introduction

Kaolin is a clay mineral which has been used since antiquity for the manufacture of ceramic utensils and containers, is currently used in multiple applications in various industries. Kaolin clay is a hydrated aluminum silicate that is the product of the decomposition of feldspathic rocks. The term generally refers to kaolin clays in compounds in which the predominant mineral is kaolinite (Al₂O₃·2SiO₂·2H₂O) [1].

The presence of impurities, particularly iron and titanium bearing materials, impart color to kaolin. During the formation of kaolin by either hydrothermal alteration or weathering, significant levels of iron oxides can be deposited on the kaolinitic clay to dramatically reduce their industrial application.

Consequently, several chemical methods have historically been applied to kaolin beneficiation in order to reduce these contaminants [2, 3-5].

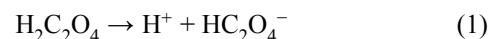
The use of different organic and inorganic acids to dissolve iron compounds using a factorial statistical design have been evaluated in several studies [3, 6] in an attempt to replace the expensive high-temperature technique of chlorination (750 °C-900 °C) [7].

Ambikadevi [8] and Martínez Luévanos [9] used various organic acids (acetic, formic, citric, ascorbic, etc.) to dissolve iron compounds and concluded that oxalic acid is the most efficient for dissolving iron oxide ceramic minerals. Oxalic acid has a lower risk of contaminating the treat-

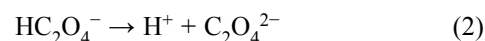
ed material after calcination, has good complexing properties, and a high reducing power compared to other organic acids.

Panias et al. [10] concluded that the dissolution of iron with oxalic acid involves three distinct processes that take place simultaneously, including: (a) the adsorption of the organic acid on the surface of iron oxide, (b) the non-reductive dissolution, and (c) the reductive dissolution.

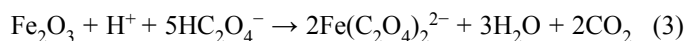
The dissolution process must also be optimized with respect to the concentration of oxalate and pH to minimize the precipitation of ferrous oxalate. Oxalic acid solution (H₂C₂O₄) ionizes to form the ion bi-oxalate (HC₂O₄⁻):



Furthermore, the formed bi-oxalate ionizes to form the oxalate ion (C₂O₄²⁻):



These two species were considered to bi-oxalate, and are responsible for the iron dissolution [4]:



Therefore, the conditions of the acid solution should be favorable for the prevalence of ion bi-oxalate HC₂O₄⁻.

We statistically treated experimental variables affecting the dissolution of iron from kaolinitic clays (e.g., acid concentration, temperature, time, and pH) to obtain a mineral useful for various industrial applications.

Results and Discussion

Mineralogical analysis

X-ray diffraction analysis revealed the nature of the crystalline phases present in the mineral as shown in Fig. 1. The study sample is mainly constituted by the kaolinite mineral with minor contributions of silica were also detected as quartz and tridymite. Iron is considered to be an impurity and is present as magnetite (Fe_3O_4),

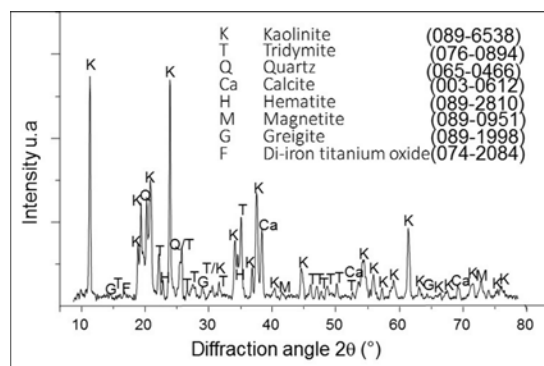


Fig. 1. X-ray diffractogram of kaolin mineral with average particle size 35 μm .

hematite (Fe_2O_3), titanium oxide-ferrous (Fe_2TiO_4), and greigite (Fe_3S_4).

It is important to make this identification because several studies [2-3, 8, 11], have reported the dissolution of magnetite, hematite, and greigite using oxalic acid, and agree that the dissolution of the hematite is much slower than the dissolution of magnetite and other hydrated iron oxides such as goethite ($\alpha\text{-FeOOH}$) and lepidocrocite ($\gamma\text{-FeOOH}$). This suggests that the use of different chemicals and experimental conditions can explain the mechanism of dissolution of hematite and magnetite.

Factorial design

The results obtained from the analysis of variance (ANOVA) in terms of iron extraction percentage were analyzed in order to determine the statistical effects of the variables investigated, as well as their interactions. The dependent variable of the process used in developing the ANOVA was the percentage yield of dissolution of iron.

Table 1 presents ANOVA results obtained from the experiments leaching iron from kaolin. This analysis demonstrated that the of temperature (b) and pH (d), and the interaction between temperature and time (bc) have a highly significant effect on the percentage of iron extraction. The concentration in this range was not significant.

Fig. 2 and 3 show the graphs of principal effects and normal effects, respectively. Concentration does not have a significant effect in the range from 0.35 M to 0.50 M; however, the effects of temperature, pH and the combined effects of temperature and time are significant.

Table 1. Analysis of variance results 24 factorial design.

Source of variation	Degrees of freedom	Sum of Squares	Adjusted sum of squares	Adjusted mean squares	Calculated F	Theoretical F $\alpha = 0.05$	Observations
principal effects	1	400.87	400.87	100.217	6.34	0.034	NS
concentration	1	2.04	2.04	2.04	0.13	0.734	NS
Temperature	1	209.49	209.49	209.49	13.24	0.015	**
Time	1	70.53	70.53	70.53	4.46	0.088	NS
pH	1	118.81	118.81	118.81	7.51	0.041	**
Interactions number of factors	6	310.57	310.57	51.76	3.27	0.107	NS
Concentration*Temperature		6.26	6.26	6.26	0.40	0.557	NS
Concentration*Time	1	2.04	2.04	2.04	0.13	0.734	NS
Concentration*pH	1	0.00	0.00	0.00	*	*	NS
Temperature*Time	1	241.67	241.67	241.67	15.28	0.011	**
Temperature*pH	1	16.89	16.89	16.89	1.07	0.349	NS
Time*pH	1	43.71	43.71	43.71	2.76	0.157	NS
residual error	5	79.09	79.09	15.82			
Total	15	790.53					

** Highly significant.

NS= not significant.

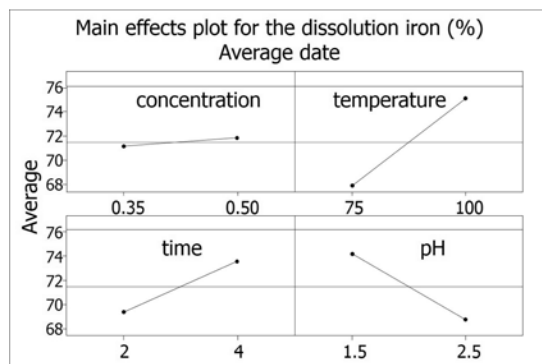


Fig. 2. Main effects plot for the dissolution iron (%).

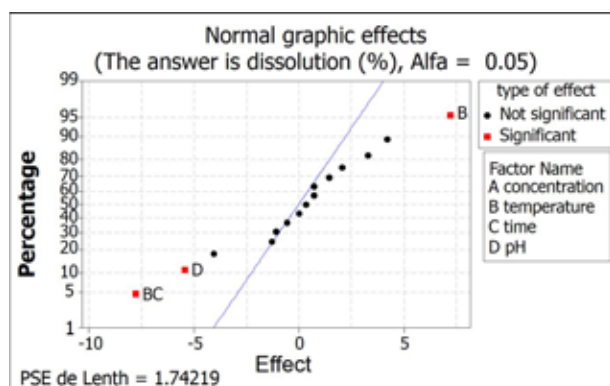


Fig. 3. Normal effects graphic.

Effect of temperature

Fig. 4 shows that iron removal increases with temperature and is greater at the temperature of 100 °C. This result is attributed to the fact that the non-reductive dissolution pathway is a simple desorption process. It involves desorption of the adsorbed surface ferric complex ions and their transfer to the acidic solution. The non-reductive dissolution mechanism removes only the more reactive sites of the oxide surface, which increases with decreasing pH and increasing temperature [10]. At temperatures below 90 °C, it is not an operative pathway and the dissolution rate is not proportional over the entire surface of the iron oxide.

Therefore, the dissolution of iron using oxalic acid must be thermally activated to be efficient. This is an indicator that the system exhibits chemical control. This result coincides with similar results obtained for other kaolinitic minerals reported in previous studies [4, 11].

Effect of concentration

Factorial design results did not show a significant effect for oxalic acid concentration. This result can be explained as follows: at the stoichiometric ratio (oxalate/iron oxide) of 5:1 as per Eq. (3), a concentration of 0.50 M represents an approximately 12-fold excess of the stoichiometric requirement for oxalate. This may be caused by the gradual formation of a passivation layer of iron oxalate $\text{Fe}(\text{C}_2\text{O}_4)(\text{s})$ with respect to time, which

is favored by the presence of soluble $\text{Fe}(\text{II})$ produced during the dissolution process that can accumulate near the reaction interface [3]. As illustrated in Fig. 5, the temperature-time relationship influences the dissolution rate of iron. At 2 h of dissolution at 75 °C and 100 °C, the percentages were 64% and 74%, respectively, whereas at 4 h, the percentages were 71% and 74%, respectively.

Effect of pH

Fig. 6 and 7 show that pH has a significant effect on the dissolution of iron, and is most evident at 2 h.

To better explain the effect of pH on iron dissolution, we developed stability and distribution diagrams (Fig. 8) and Eh-pH diagrams (Fig. 9) using the software Medusa (Chemical Equilibrium Diagrams).

As described above, the species responsible for iron dissolution is the bi-oxalate (HC_2O_4^-) ion according to equation (3). As shown in Figure 8, the distribution of three species of oxalic acid at a concentration of 0.35 M (i.e. $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- , and $\text{C}_2\text{O}_4^{2-}$), where the HC_2O_4^- ion is the predominant species in the pH range 2.5-3.0, explains why the reaction rate increases over this pH range. This coincides with previous results [4, 9, 11], in which a change in predominance was not due to acid concentration.

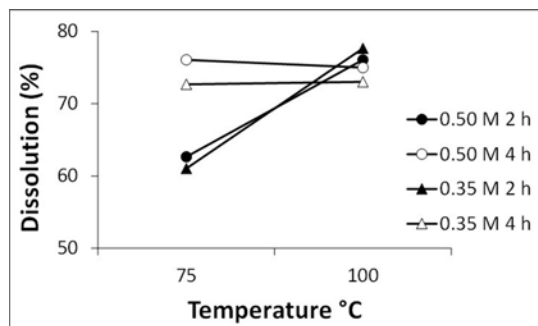


Fig. 4. Effect of temperature on the dissolution of iron.

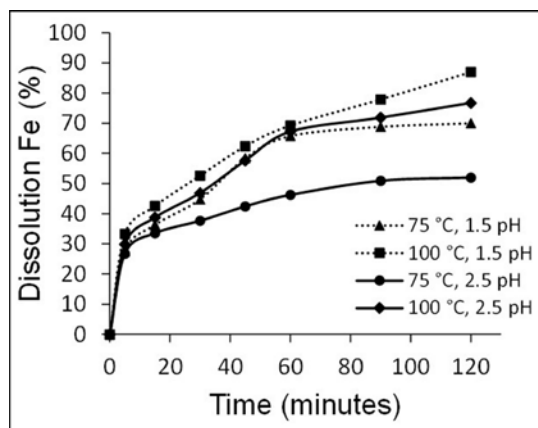


Fig. 5. Effect Temperature-Time on the dissolution of iron. 0.5 M concentration oxalic acid, pH 2.5.

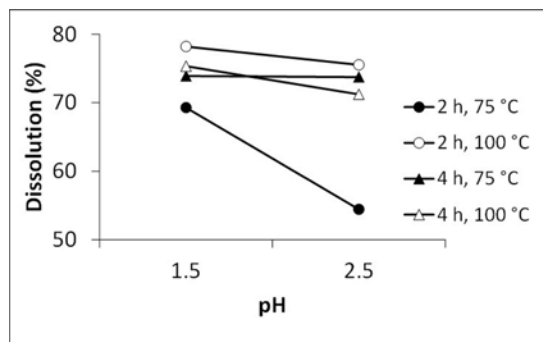


Fig. 6. Effect of pH on the dissolution of iron.

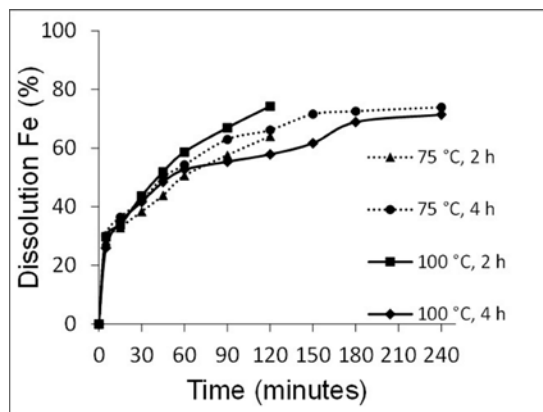


Fig. 7. Effect of pH on the dissolution of iron. 0.35 M oxalic acid concentration. 2 h.

pH values of 1.5 and 2.5 were examined, and we found that the fractions of bi-oxalate (HC_2O_4^-) were 70% and 90%, respectively. This indicates that the best results are obtained at a pH of 2.5, resulting in a largely dissociated oxalic acid. In developing the Eh-pH diagram shown in figure 9, however, the level of Fe used in this study (0.0087 M total Fe) hindered the solution because of the presence of solid $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{s})$, which shows a passivation mechanism due to the formation of this solid on the oxide surface and is governed by its precipitation from solution [4]. For a pH of 1.5, the solid is stable over a pH range of 1.14-2.80. At a pH of 2.5, the range is 1.12-2.80. Therefore, at a pH of 1.5, only 70% dissociation of oxalic acid is obtained as it is close to the zone of stability of the Fe^{2+} and away from the zone of formation of solid $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{s})$.

At a pH of 2.5, the dissociation of oxalic acid was more than 90%; however, this is further away from the zone of stability for Fe^{2+} and is well within the zone of stability of solid $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{s})$.

Whiteness index

Figure 10 shows the percentage of dissolved iron, and the index or ratio of whiteness obtained using an oxalic acid concentration of 0.35 M, pH 1.5, 100 °C, and time of 2 h. The whiteness index increases with the same trend as that observed for the dissolution of iron, yielding a maximum whiteness index

of 93.55%. This result confirms that the decrease in the percentage of iron oxides in the mineral increases the whiteness index [4].

Experimental

Reagents and materials

The kaolin mineral sample was obtained from Agua Blanca de Iturbide, Hidalgo (Mexico), which was previously reduced in size and classified by ASTM mesh. Mineral particles of an average size of 35 μm were used in the leaching experiment. A complete chemical analysis by atomic absorption spectrophotometry is shown in Table 2. The iron content in the mineral was 0.70 ± 0.01 % (iron content in the minerals was 0.506 % Fe and is reported as Fe_3O_4 with a value of 0.70 %). Oxalic acid (reagent-grade; Aldrich, St. Louis, MO, USA) was used as a leaching agent. The leaching system used consisted of a heating

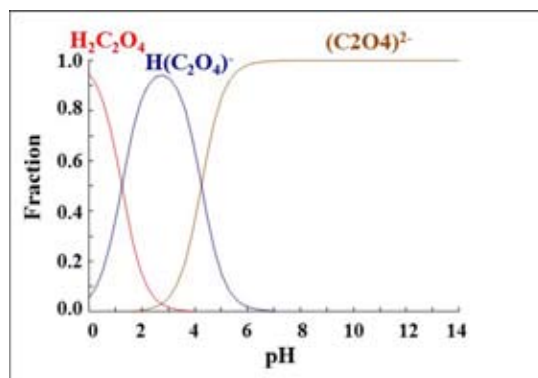


Fig. 8. Speciation of various oxalate species at 0.35 M oxalic acid.

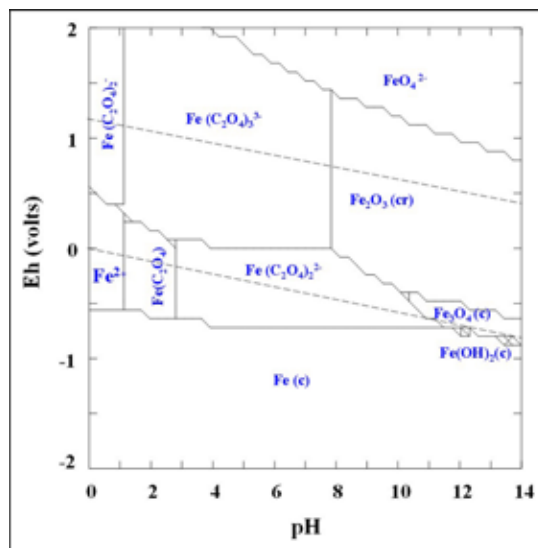


Fig. 9. Eh-pH diagrams of Fe-oxalate system at 0.35 M oxalate and 0.0087 M total Fe.

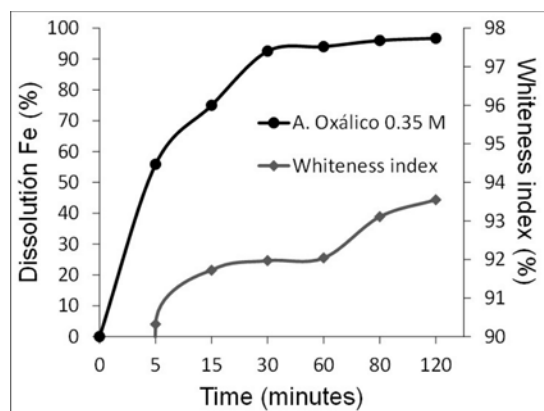


Fig. 10. Dissolution of iron and whiteness index obtained at a concentration of 0.35 M oxalic acid, pH 1.5, 100 °C for a time of 120 minutes.

Table 2. Chemical analysis of the kaolin sample.

Components	Wt [%]
SiO ₂	65.00
Al ₂ O ₃	27.00
Fe ₃ O ₄	0.70
CaO	0.04
MgO	0.57
Na ₂ O	2.65
K ₂ O	2.42
TiO ₂	0.67
LIO*	0.95

LIO* = Loss of ignition

mantle, a Pyrex glass reactor of 500 mL with a condenser, and magnetic stirring. A centrifuge was used (Model 228, Fisher Scientific, Waltham, MA, USA) for solid-liquid separation of the sample collected for quantification of dissolved iron. Iron was quantified using atomic absorption spectrophotometry (Optima 3000 XL, Perkin Elmer Waltham, MA, USA). To determine the mineral species present in the kaolin samples a X-ray diffraction patterns were determined using an Equinox 2000, Inel, Artenay, France, diffractometer with Cu K α radiation at 40 kV and 40 mA. The whiteness index was determined using reflectance spectrophotometry (XTS Color Eye Software, GretagMacbeth).

Experimental design

Leaching experiments were carried out according to a 2⁴ factorial design with two replicates. The independent variables included the concentration of oxalic acid (0.35 and 0.50 M), temperature (75 °C and 100 °C), extraction time (2 and 4 h), and pH (1.5 and 2.5). The dependent variable was the percent-

Table 3. Factors and levels used in the ANOVA.

	Factor	Units	Levels	
			+	-
a	H ₂ C ₂ O ₄	M	0.35	0.50
b	Temperature	°C	75	100
c	Time	Hours	2	4
d	pH		1.5	2.5

age of dissolved iron. The factors and the levels investigated are shown in Table 3 and the treatments of the factorial experiment are shown in Table 4.

Leaching of kaolin

Leaching experiments were carried out in a 500 mL round bottom glass reactor. Stirring was conducted magnetically and at constant temperature. In leaching tests at 100 °C, the reactor, equipped with a thermometer and a reflux condenser, was heated with a thermostatically controlled heating mantle. All leaching tests were conducted at atmospheric pressure. For each run, 400 mL of oxalic acid solution (C₂H₂O₄), reagent grade) was added to the reactor and the temperature was set to the desired value. Next, 40 g of clay are added to the reactor while under 700 rpm magnetic stirring. Periodically (5, 15, 30, 60, 90, 120, 150, 180, 210, and 240 min), a 10 mL sample was taken from the leach slurry and filtered using a vacuum, and then centrifuged immediately at 300 rpm for 15 min. A clear 5-mL aliquot of the solution was collected for total iron determination. In all experiments, we used a solid-liquid ratio of 10 g of kaolin and 100 mL of leaching solution. Experiments were performed in duplicate.

Conclusions

In this study, a factorial design was used to examine the dissolution of iron by oxalic acid. Experimental results were used to determine the main effects and interactions of the factors investigated. We found that temperature and pH strongly influenced iron dissolution; temperature-time interactions had a less significant influence. Furthermore, the concentration of oxalic acid showed a slight effect on iron extraction, which was attributed to the formation of Fe(C₂O₄)(s). This results in a passivation mechanism due to the formation of this solid on the surface of iron oxide or is governed by its precipitation from the bulk solution. It was confirmed that decreasing the percentage of iron oxides increases whiteness index.

The best results were obtained under the following experimental conditions: removal of 88% iron and whiteness index of 93.50% at 100 °C, 0.35 M oxalic acid, and pH 1.5 over a time period of 2 h.

Table 4. Treatments of the full factorial design.

Treatments	a	b	c	d	Label	a	b	c	d	Combinations	Dissolution Fe (%)
1	-	-	-	-	(1)	0	0	0	0	a1b1c1d1	69.98
2	+	-	-	-	a	1	0	0	0	a2b1c1d1	68.55
3	-	+	-	-	b	0	1	0	0	a1b2c1d1	87.00
4	+	+	-	-	ab	1	1	0	0	a2b2c1d1	75.00
5	-	-	+	-	c	0	0	1	0	a1b1c2d1	71.77
6	+	-	+	-	ac	1	0	1	0	a2b1c2d1	76.06
7	-	+	+	-	bc	0	1	1	0	a1b2c2d1	74.98
8	+	+	+	-	abc	1	1	1	0	a2b2c2d1	75.70
9	-	-	-	+	d	0	0	0	1	a1b1c1d2	52.00
10	+	-	-	+	ad	1	0	0	1	a2b1c1d2	64.00
11	-	+	-	+	bd	0	1	0	1	a1b2c1d2	76.77
12	+	+	-	+	abd	1	1	0	1	a2b2c1d2	74.27
13	-	-	+	+	cd	0	0	1	1	a1b1c2d2	73.55
14	+	-	+	+	acd	1	0	1	1	a2b1c2d2	73.91
15	-	+	+	+	bcd	0	1	1	1	a1b2c2d2	97.00
16	+	+	+	+	abcd	1	1	1	1	a2b2c2d2	71.41

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