BUREAU OF ECONOMIC GEOLOGY

Geological Circular 65-1

Bloating Characteristics of East Texas Clays

By

W. L. Fisher and L. E. Garner

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BLOATING CHARACTERISTICS OF EAST TEXAS CLAYS

W. L. Fisher and L. E. Garner

Abstract

Incidence of bloating among approximately 600 clay samples from East Texas, ranging in age from Gulfian (Late Cretaceous) to Recent, correlates principally with clay mineralogy and pH--together an indication of bulk composition--and to a lesser extent with texture, loss on ignition, and content of nonclay refractory minerals. Clay-mineral and pH data permit prediction of bloating with an accuracy of about 80 percent. Montmorillonitic and illitic clays are the best bloaters; bloating occurs in more than 80 percent of clays consisting of less than 30 percent kaolinite, more than 10 percent illite, and between 20 and 90 percent montmorillonite. Only 10 percent of the high-alumina clays (more than 50 percent kaolinite) bloat; these generally are plastic and carbonaceous. Value of pH is an index of the amount of certain flux and gas-forming materials in clays; accordingly, bloating incidence generally increases with increase in pH. Incidence of bloating also increases slightly with decrease in grain size, increase in plasticity, increase in loss on ignition, and decrease in content of nonclay refractory minerals.

Introduction

Under certain conditions of firing, some clays expand to form a material with density lower than the unfired clay. For such a bloating reaction: (1) compounds that liberate gases during firing must be present in the clay, and (2) a portion of the clay must fuse or vitrify during firing to form a substance sufficiently viscous to trap the gases. Dissociation of minerals and formation of gases must occur when the clay is in the pyroplastic state.

In standard ceramic processes, bloating is an undesirable reaction. Since about 1915, however, clays that bloat or expand upon firing have been used in the manufacture of lightweight aggregate. In recent years, lightweight clay aggregate has been used increasingly in both load-bearing and nonload-bearing concrete castings and forms. Approximately 7.6 million tons of lightweight clay aggregate, marketed under such trade names as Haydite, Featherlite, Billite, were produced in the United States during 1964. Texas annually produces about 0.8 million tons of lightweight clay aggregate.

The purpose of this study is to correlate bloating incidence with certain physical and mineralogical properties of a wide variety of clays, and to utilize this correlation as a simple tool in the exploration of clays suitable for manufacture of lightweight aggregate. Correlations are based on laboratory tests and study of the bloating and nonbloating characteristics of approximately 600 clays sampled from an area of about 35,000 square miles in East and Northeast Texas (fig. 1).

Acknowledgments

We express appreciation to the following persons for reading the manuscript and offering helpful criticisms: Peter T. Flawn, Peter U. Rodda, and Josephine Casey, Bureau of Economic Geology, The University of Texas, and E. C. Jonas, Department of Geology, The University of Texas. Most of the laboratory tests were made under the direction of D. A. Schofield, Mineral Studies Laboratory, Bureau of Economic Geology. Samples were collected chiefly by J. G. Frost and J. H. McGowen.

Sampling and Testing Procedures

Samples investigated in this study were collected as a part of a regional inventory of resources in East Texas and were collected as clays potentially suitable for a number of uses in addition to that of lightweight aggregate (Fisher et al., in press). Samples were obtained from active and abandoned clay pits, road cuts, shallow auger holes, and natural exposures.

Fired specimens were prepared by grinding the raw clay to -20 mesh and extruding a stiff mud through a $\frac{1}{2}$-inch, circular die. Discs were wire-cut into $\frac{1}{4}$-inch lengths, air-dried for 12 hours, and oven-dried at 105°C (221°F) for 1 hour. Dry discs were preheated at 300° to 350°C (572° to 662°F) for 30 minutes in an electric muffle furnace, thence immediately transferred to another muffle furnace and flash fired for 10 minutes at temperatures of 2000°, 2200°, and 2400°F. A series of 6 liquids (n-heptane, kerosene, water, carbon disulfide, chloroform, and carbon tetrachloride) ranging in specific gravity from 0.7 to 1.6 were used to determine bulk specific gravity of fired discs.

Clay mineral composition of the -5 micron fraction was determined by X-ray diffraction techniques, using a G. E. XRD 6 diffractometer with nickel-filtered copper radiation generated at 35 kv and 16 ma. Method of calculating percent of specific clay minerals was a modification and simplification of procedures outlined by Freas (1962), in which height of intensity peaks was used rather than the area of peaks. Peak heights recorded from diffractograms made from oriented slides (001) were corrected by use of a factor of 2 for kaolinite, 3 for illite, and 3 for montmorillonite. Percent of each clay mineral was calculated as a percent of the total of corrected heights. Disoriented clays were glycolated to arrange properly the illite and montmorillonite fractions. Other clay tests, such as plasticity, loss on ignition, and pH, were made in accordance with procedures outlined by the U. S. Bureau of Mines (Klinefelter and Hamlin, 1957).

Stratigraphic Distribution

East Texas clays range in age from Late Cretaceous to late Cenozoic (fig. 2). They are diverse in origin and mineral composition but can be grouped generally into three main divisions (fig. 3): (1) Late Cretaceous (Eagle Ford, Austin, Taylor, and Navarro Groups) and early Paleogene (Midway Group) marine, montmorillonitic clays; (2) early and middle Paleogene (Wilcox and Claiborne Groups) mostly nonmarine, kaolinitic-illitic clays; and (3) late Paleogene (Claiborne and Jackson Groups, Catahoula Formation) and early Neogene (Fleming, Willis, and Lissie Formations) marine to mostly nonmarine, montmorillonitic, bentonitic clays.

Montmorillonite is the dominant clay mineral in Upper Cretaceous and Midway clays and in upper Claiborne and younger clays where montmorillonite is commonly associated with deposits of bentonite and volcanic ash. Kaolinite is characteristic of the Wilcox and lower Claiborne Groups and is most abundant among nonmarine and deltaic sediments. Illite, occurring in amounts generally less than 30 percent, is a common constituent in rocks of the Midway and Wilcox Groups; it is progressively less common among younger rocks. Illite occurs in greatest concentrations in the Midway and Wilcox Groups in the eastern part of the area, chiefly on the south side of the Sabine Uplift.

Bloating Factors

A number of factors determine the bloating characteristics of clays, including clay mineralogy, accessory nonclay mineral composition, chemical composition, pH, texture, particle size, and particle size distribution. These vary in significance and importance from one clay to another; no one set of conditions or combination of factors hold invariably. Variations in preparation and firing of clays also alter bloating characteristics.

Mechanisms involved in and factors controlling bloating of clays have been investigated in a number of studies: Austin et al. (1942), Burwell (1954), Cole and Zetterstrom (1954), Conley et al. (1948), Ehlers (1958), Everhart et al. (1958), Greaves-Walker et al. (1951), Herold et al. (1958), Mason (1951), Mielenz and King (1955), Murray and Smith (1958), Parks et al. (1964), Plummer and Hladik (1951), Prokopovich and Schwartz (1957), Riley (1951), Sullivan et al. (1942), and White (1960). Most of these were based on studies of Paleozoic clays and shales (predominately illitic and kaolinitic) of the central United States.

Clay mineral composition.--Kaolinitic clays are largely aluminum silicates and generally too refractory to bloat at standard firing temperatures. Montmorillonitic and illitic clays contain magnesium, calcium, potassium, and sodium as essential parts of their structures and are good bloaters. Average ratios of illite plus montmorillonite to kaolinite among East Texas clays is 4.5 for those bloating and 0.7 for those failing to bloat. Ehlers et al. (1958, p. 37) reported average ratio of illite to kaolinite for Ohio bloating clays of 2.7 and for nonbloating clays, 1.6.

East Texas illitic clays have a high incidence of bloating with bloating in 90 percent of those containing illite in excess of 50 percent (figs. 4, 5). Bloating occurs in 70 percent of clays containing montmorillonite in excess of 50 percent (figs. 4, 5). Less than 10 percent of the clays containing more than 50 percent kaolinite will bloat (figs. 4, 5). Bloating incidence ranges from about 40 to 60 percent in clays containing approximately equal amounts of kaolinite, montmorillonite, and illite. Number of bloating clays progressively increases with increase in content of montmorillonite up to 50 percent; a larger content of montmorillonite does not increase the probability of bloating. Kaolinite content of less than 20 percent or more than 60 percent has little effect on bloating incidence; between the range of 20 to 60 percent, bloating incidence progressively decreases with increase in content of kaolinite (fig. 5).

No correlation is obvious between bloating incidence and degree of clay mineral crystallinity.

Fluxing and gas-forming components.--Requirements for bloating are the presence of components in proper proportions to serve as fluxing and gas-forming agents. These occur (1) as essential or exchangeable cations in the clay structure, or (2) as accessory, nonclay compounds associated with clay minerals. In the first case, clay mineral composition is an index to bloating; in the second, bloating correlates with bulk mineral composition.

The most common fluxing agents in bloating clays are (expressed as oxides) CaO, MgO, K_2O, Na_2O, FeO, and Fe_2O_3. These determine the temperature range and character of the viscous (pyroplastic) state. For commercial bloating clays, the viscous state should develop within the range of 2000° to 2400°F and should persist through a range of about 200°F; accordingly, the specific type and amount of fluxing agent are important in developing suitable viscosity at proper temperature ranges. Excessive fluxing components produce a melt below the 2000° to 2400°F range or result in a melt insufficiently viscous to trap liberated gases; low content of fluxes prevents fusion within this range.

Riley (1951) estimated limits of fluxing components (exclusive of volatile and minor constituents and expressed as oxides) necessary to produce a viscous material within the 2000° to 2400°F range as about 25 to 40 percent. Subsequent investigations generally have supported the conclusions of Riley, although limits in range of fluxing components have been modified slightly (e.g., White, 1960, p. 14). The type of fluxing agent should be considered, as some fluxes are much stronger than others; further, refractory clay minerals (e.g., kaolinite) require larger amounts of fluxes to develop suitable viscosity at standard temperatures. Calcium is a very active flux and generally causes a short vitrification range. Its presence, however, increases significantly the incidence of bloating of clays flash fired at temperatures of 2000° and 2200°F. East Texas calcareous clays bloat at a rate of 2.5 times that of noncalcareous clays (table 1); at 2400°F, however, melting generally occurs, and bloating incidence of calcareous clays is considerably lower than noncalcareous clays. Calcium occurs in East Texas clays as a component of the clay structure, in which case it is a flux and as free calcium carbonate, which is a source of gas; most of the calcareous clays are montmorillonites. The high incidence of bloating among illitic clays is a result of potassium, an element essential to the illite structure. A moderate amount of potassium in a clay broadens the range of vitrification, increases the

Table 1. Relationship of calcium (expressed as an oxide) content and bloating incidence, East Texas clays. (Data for calcareous clays based on 30 samples, non-calcareous clays based on 500 samples; values in table are percent of total sample for indicated content of CaO.)

	Flash fired at 2000°F			Flash fired at 2200°F			Flash fired at 2400°F		
	CaO $>5\%$	CaO 1-5%	CaO 0%	CaO $>5\%$	CaO 1-5%	CaO 0%	CaO $>5\%$	CaO 1-5%	CaO 0%
Light bloating (sp. gr. <1.5)	0	0	--	23	77	--	14	46	--
Heavy bloating (sp. gr. >1.5)	15	3	--	45	8	--	9	0	--
Total bloating	15	3	3	68	85	28	23	46	90
Melted	0	0	0	14	4	0	68	54	2
Not bloating	85	97	97	18	11	72	9	0	8

range in which the viscous clay is capable of entrapping liberated gases, and thereby increases bloating possibilities (Grim, 1962, p. 355). Presence of fluxing elements as exchangeable cations and as parts of the structure of montmorillonite partly accounts for the high incidence of bloating among these clays. Kaolinitic clays generally are low in fluxing elements as these are not essential parts of the kaolinite structure. Further, kaolinites commonly were formed under acidic or leaching conditions so that fluxes in the form of accessory minerals commonly are removed.

Distribution of fluxes within clay materials is also significant in the formation of a melt proper for bloating. Fluxing agents as exchangeable or essential cations to the clay structure, as well as uniformly distributed, fine-grained accessory particles, contribute to uniform melting and development of a consistent and uniform viscous mass. Fluxing materials occurring as nodules or poorly distributed particles (e. g., calcareous concretions) cause strong fluxing action immediately adjacent to the nodule or particle but not throughout the clay.

The second requisite in the formation of a bloating clay is the liberation of gases while the clay is in a viscous state. Exchangeable or essential cations of the clay structure are the most likely fluxing agents; accessory or nonclay components in clay materials are the significant sources of gases. Common constituents that are sources of gases at or below the upper limit of standard bloating temperatures include dolomite, calcite, pyrite, hydrated iron oxides, iron carbonates, carbonates of alkalies and alkaline earths, sulfates, adsorbed and detrital organic matter, and complex silicates, such as clay minerals, micas, and amphiboles. Gases and volatiles identified in the firing of clays include H_2O, CO_2, CO, SO_2, O_2, H_2, and H_2S. Gases are liberated through (1) decomposition and dissociation of gas-forming constituents during the viscous state (between 2000° and 2400°F), or (2) decomposition of gas-forming constituents at lower temperatures provided the low-temperature gas is retained by combination with a higher temperature material or is retained by the physical imbalance caused during flash firing. Carbon dioxide is a common gas reported in the vesicules of bloated clays and apparently evolved either through the dissociation of calcium carbonate or through the reduction of ferric oxide and combination of liberated oxygen with organic carbon.

Clay pH.--The role of pH in bloating is significant in that it is an empirical indication of the amount of potential flux and gas-forming materials in the clay. Little data have been published regarding the correlation of pH and bloating incidence, though the results of Conley et al. (1948) are commonly cited. Of 81 clay samples reported by these writers, only about 15 percent of those with pH below 5.0 bloated compared to 75 percent bloating with pH above 5.0. They reported average pH of nonbloating clays as 4.4 and bloating clays as 6.6. Our studies show a similar relationship of pH and bloating but with generally a greater proportion of bloaters among clays with lower pH (less than 5.0) and lower bloating incidence among clays of higher pH (more than 5.0) (figs. 6, 7).

Results of Conley et al. (1948) and of our studies show a general increase of bloating incidence with increase in pH; highest percent of bloating occurs among the slightly alkaline clays (pH range of 7 to 8). A slight decrease occurs among clays with pH in excess of 8; in our study most failures of the more alkaline clays (pH greater than 8.0) to bloat were due to melting within the 2000° to 2400°F firing range. Although bloating incidence is highest among low alkaline clays (pH 7.0 to 8.0), the change from lower to higher bloating incidence occurs within the pH range of 4.0 to 6.0 rather than at neutral pH (fig. 7). Only a very slight increase in proportion of bloaters with increase in pH occurs in the range of slightly acidic clays (in our study between pH range of about 4 to 6 and in the study of Conley et al. between pH range of 5 to 7). This slight exception to the otherwise progressive increase in bloating with increase in pH is not understood.

Clay mineral content influences the role of pH especially among the more acidic clays (fig. 8). Kaolinitic clays, for example, generally have lower pH values than other common clay types because of low content of soluble components. They are refractory as they have a relatively high content of alumina and generally are poor bloaters at standard firing temperatures. In our study, less than 10 percent of the clays containing more than 50 percent kaolinite bloated, whereas generally more than 40 percent of the clays with less than 50 percent kaolinite bloated. Kaolinitic clays make up about 40 percent of the clays with pH less than 5.0 and only 15 percent of those with pH greater than 5.0. Also, bloating incidence is low among kaolinitic clays regardless of pH (fig. 8). Accordingly, abundance of kaolinitic clays with low pH contributes to low bloating incidence among acidic clays; a similar situation is indicated in data reported by Conley et al. (1948). Correlation of bloating incidence and pH is most significant among montmorillonitic and illitic clays with pH greater than 7.0 (fig. 8).

Clay texture.--Textural properties of clays, such as plasticity, grain size, particle size distribution, and lamination, play a minor though, in some cases, significant role in determining bloating characteristics. Mielenz and King (1955) have indicated that probability of bloating is increased by a dense, relatively impervious fabric which resists shrinkage during heating and inhibits escape of gases before fusion. White (1960) has shown that laminated shales bloat better than massive clays and that bloating is greatest perpendicular to the laminations; apparently, the lesser permeability of laminated clays prevents easy entrance of oxygen and escape of reaction gases. Bloating incidence of East Texas clays increases generally with increase in plasticity and decrease in mean grain size (fig. 9). The few highly kaolinitic clays from East Texas that bloat are also very fine grained, plastic, and commonly contain organic material. Particle size distribution of the fluxing materials as well as the clay constituents is important in controlling uniformity of fluxing and uniformity of the expanded clay.

Loss on ignition.--Common gases and volatiles evolved during heating (loss on ignition) include carbon dioxide, water, hydrogen sulfide, and sulfur oxides. Ignition loss of East Texas clays within the temperature range of 105° to 1050°C (221° to 1922°F) varies from about 2 to 20 percent, with highest losses occurring among clays high in content of calcium carbonate. Most East Texas clays have ignition losses of 3.5 to 7.5 percent. No obvious correlation exists between percent of ignition loss and bloating incidence, except for high incidence of bloating among the highly calcareous clays (fig. 10).

Conclusions

Relatively simple and rapid tests, short of actual firing, can be used in the preliminary evaluation of clays as sources of bloating clay or lightweight aggregate. Use of bloating field diagrams (figs. 11, 12), based on clay mineralogy and pH, allows prediction of bloating or nonbloating of random samples of East Texas clays with an accuracy of about 80 percent. Accuracy of predictions among clays composed largely of a single clay mineral approaches 100 percent; by contrast, accuracy is less among clays of mixed mineral composition. Although no single factor controls bloating in all clays, bulk composition (clay and accessory minerals) is the best general index. Bulk composition is most rapidly approximated by determining clay mineral composition, which indicates proportion of aluminum silicates and exchangeable cations, and clay pH, which is a general index of the amount of potential flux and gas-forming materials.

Correlation of bloating with clay properties shown for East Texas clays should be applicable to Upper Cretaceous and Cenozoic clays of the northern and western Gulf Coastal Plain. Clays throughout the Coastal Plain are similar in range of composition, occurrence, and origin to those of East Texas.

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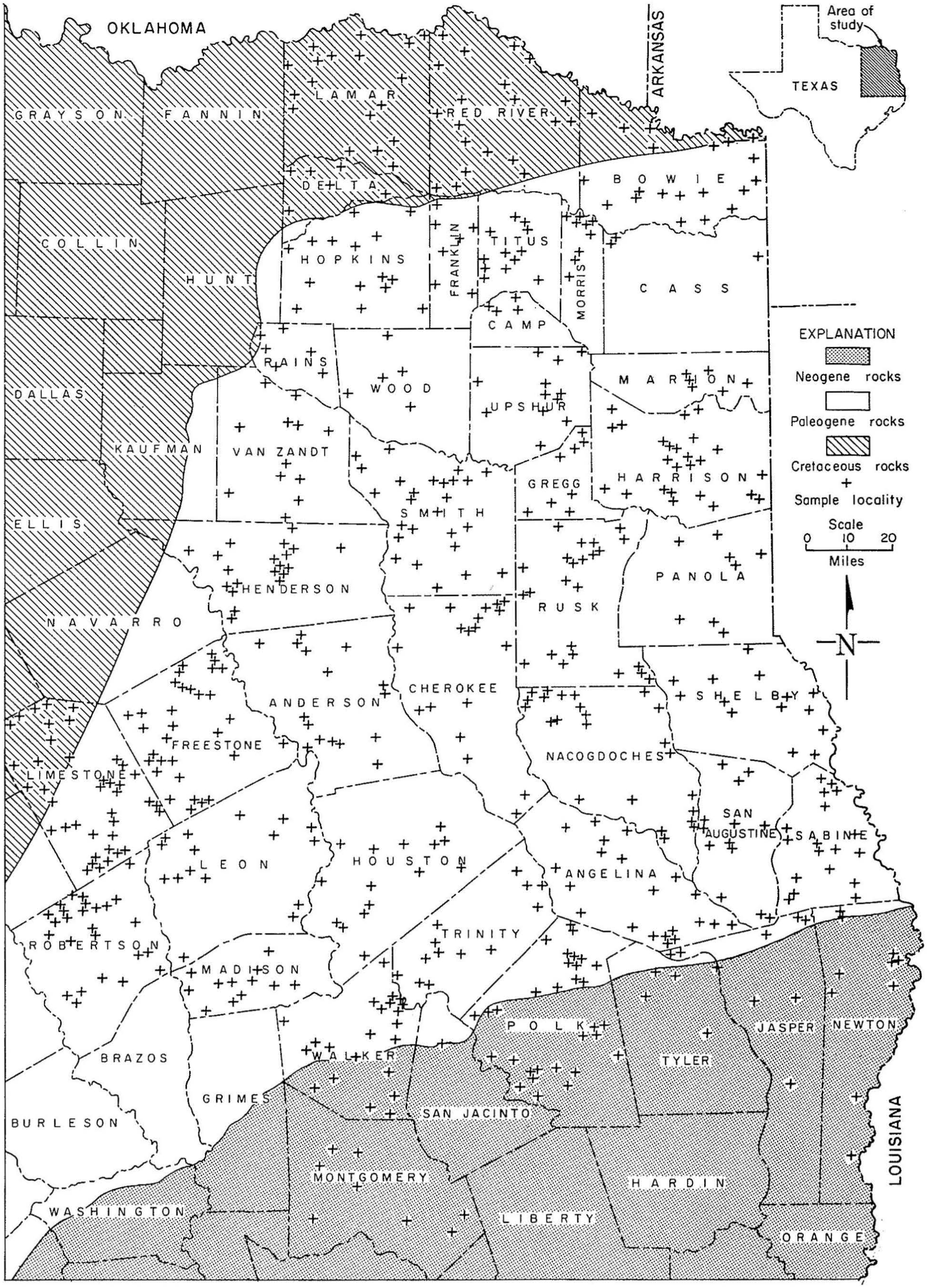


FIG. 1. Index map and distribution of clay samples.

STRATIGRAPHIC UNIT		NUMBER OF SAMPLES
NEOGENE	Lissie Formation	2
	Willis Formation	2
	Fleming Formation	27
PALEOGENE	Catahoula Formation	16
	Jackson Group	50
	Yegua Formation	15
	Cook Mountain Formation	45
	Sparta Formation	14
	Therrill Formation	6
	Weches Formation	3
	Queen City Formation	90
	Reklaw Formation	33
	Carrizo Formation	4
	Wilcox Group	203
	Midway Group	25
CRETACEOUS	Navarro Group	8
	Taylor Group	15
	Austin Group	6
	Eagle Ford Group	4

FIG. 2. Stratigraphic distribution of clay samples.

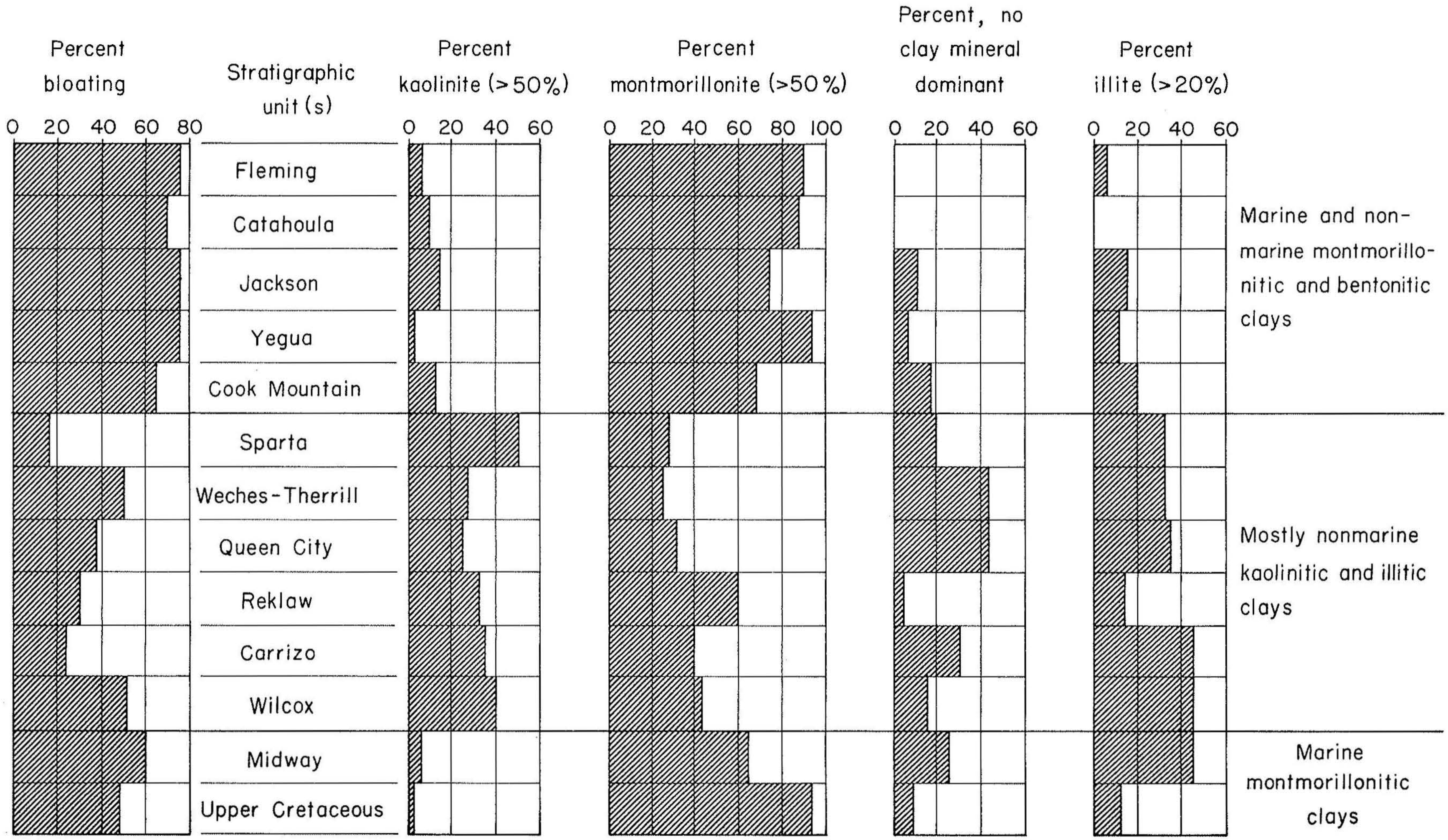
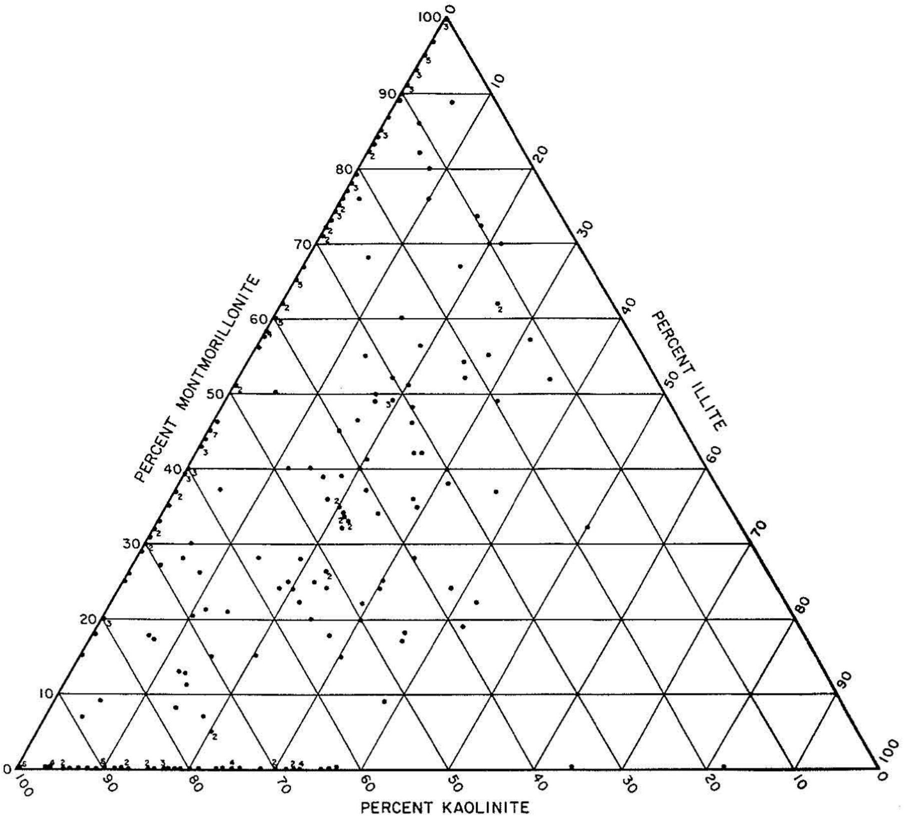
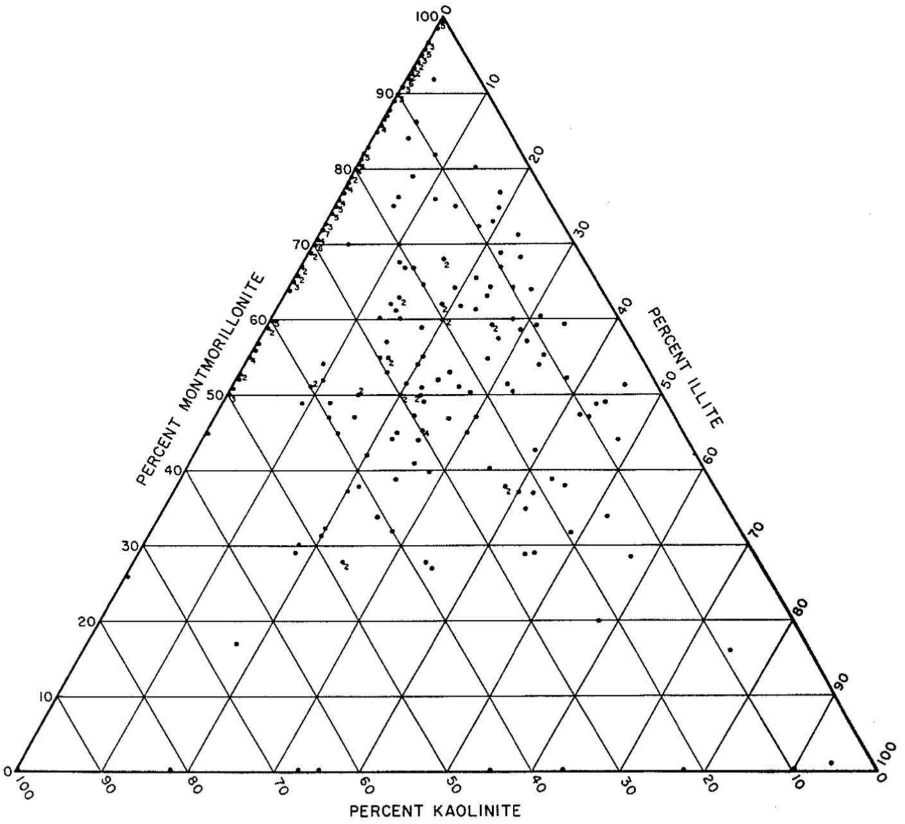


FIG. 3. Stratigraphic variation in clay mineral composition.



NONBLOATERS



BLOATERS

FIG. 4. Clay mineral composition of East Texas clays.

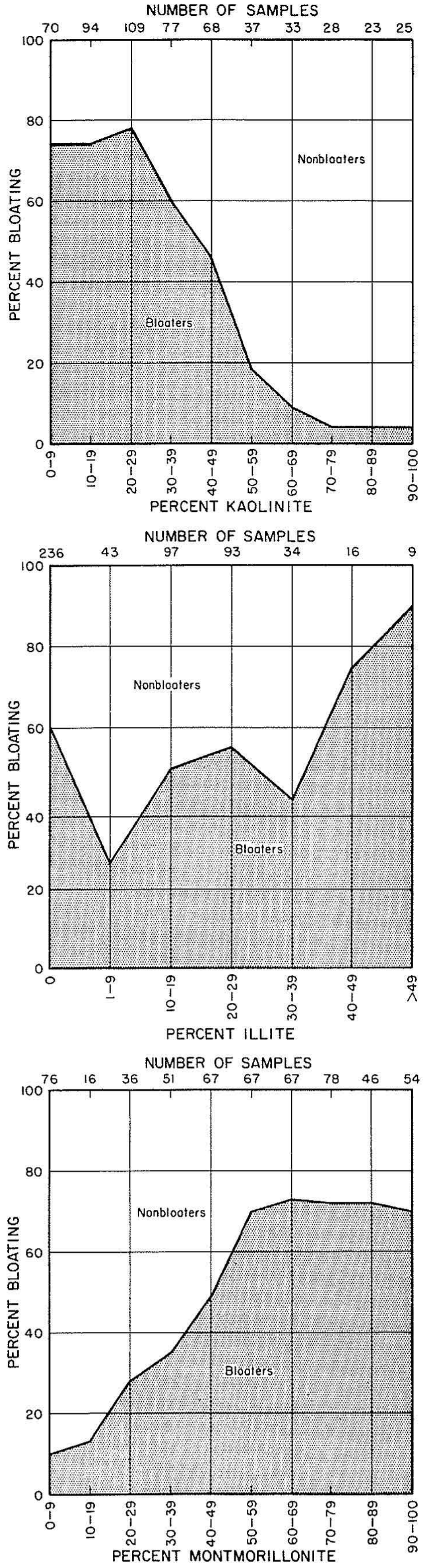


FIG. 5. Correlation of bloating incidence and clay mineral composition.

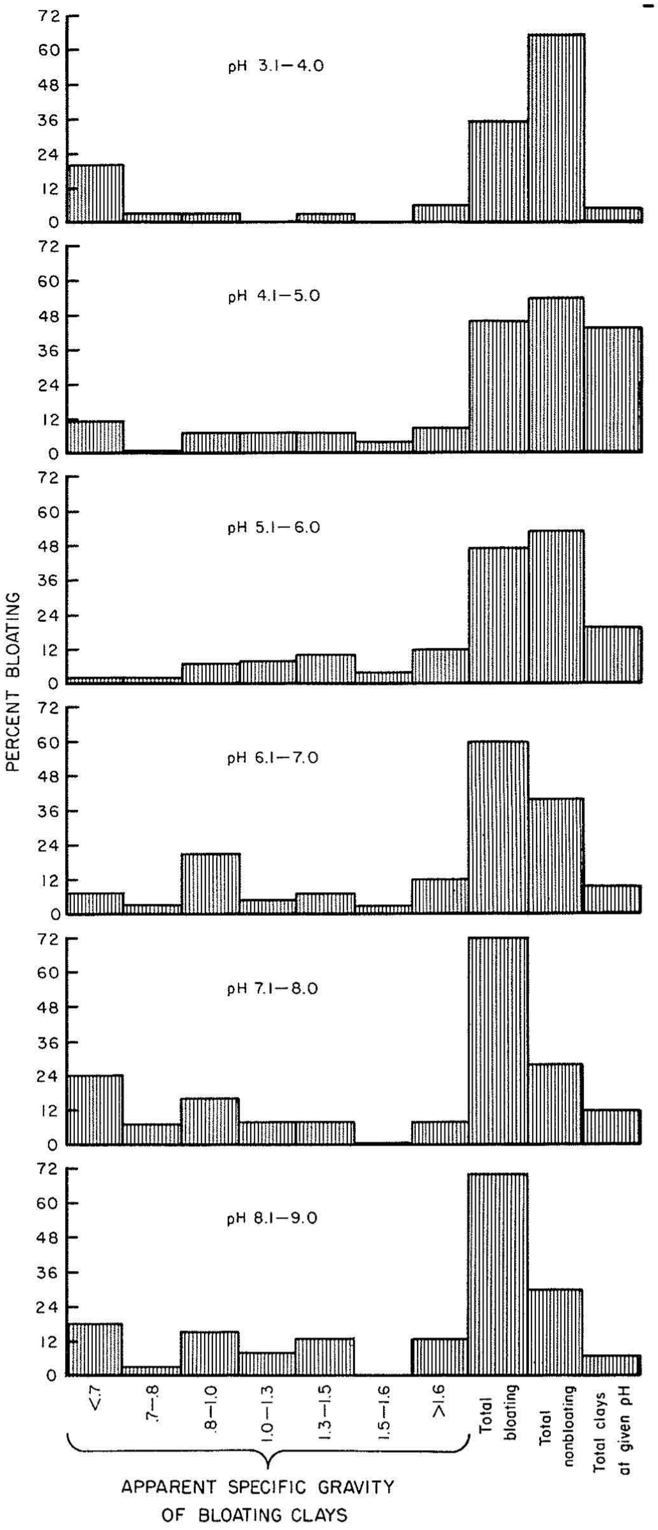


FIG. 6. Correlation of bloating incidence and clay pH.

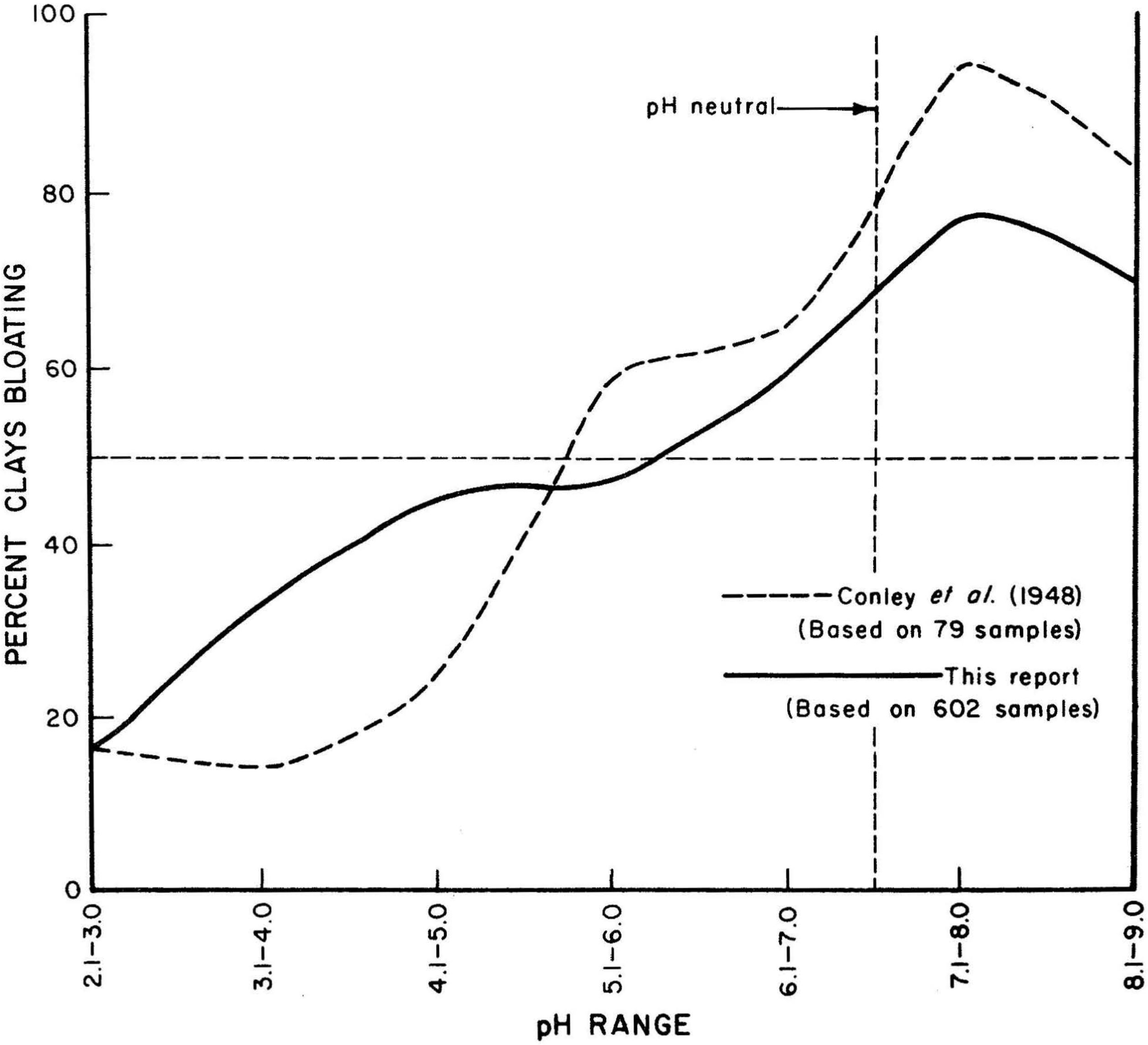


FIG. 7. Bloating incidence as a function of pH range.

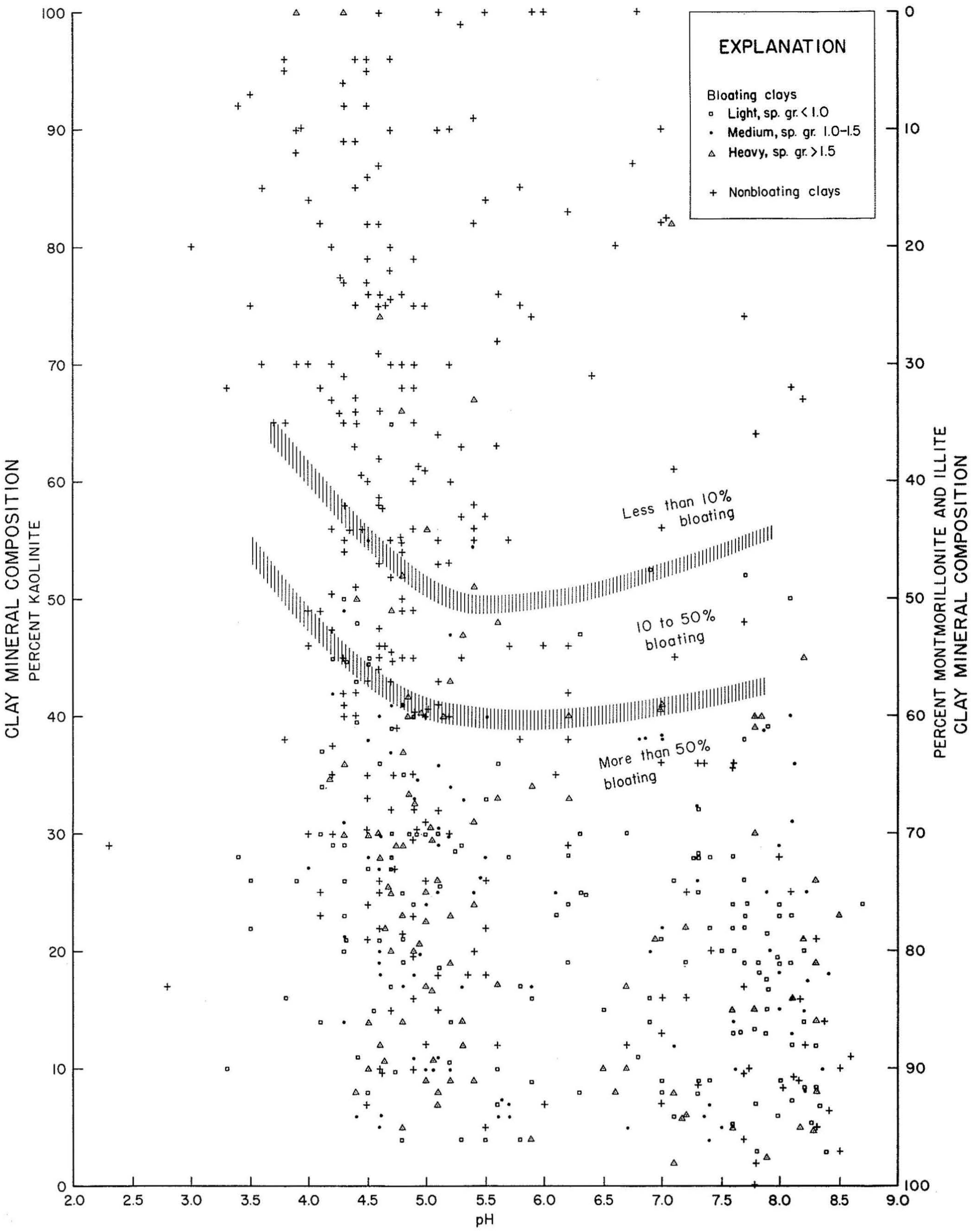


FIG. 8. Clay mineral composition and pH of bloating and nonbloating clays.

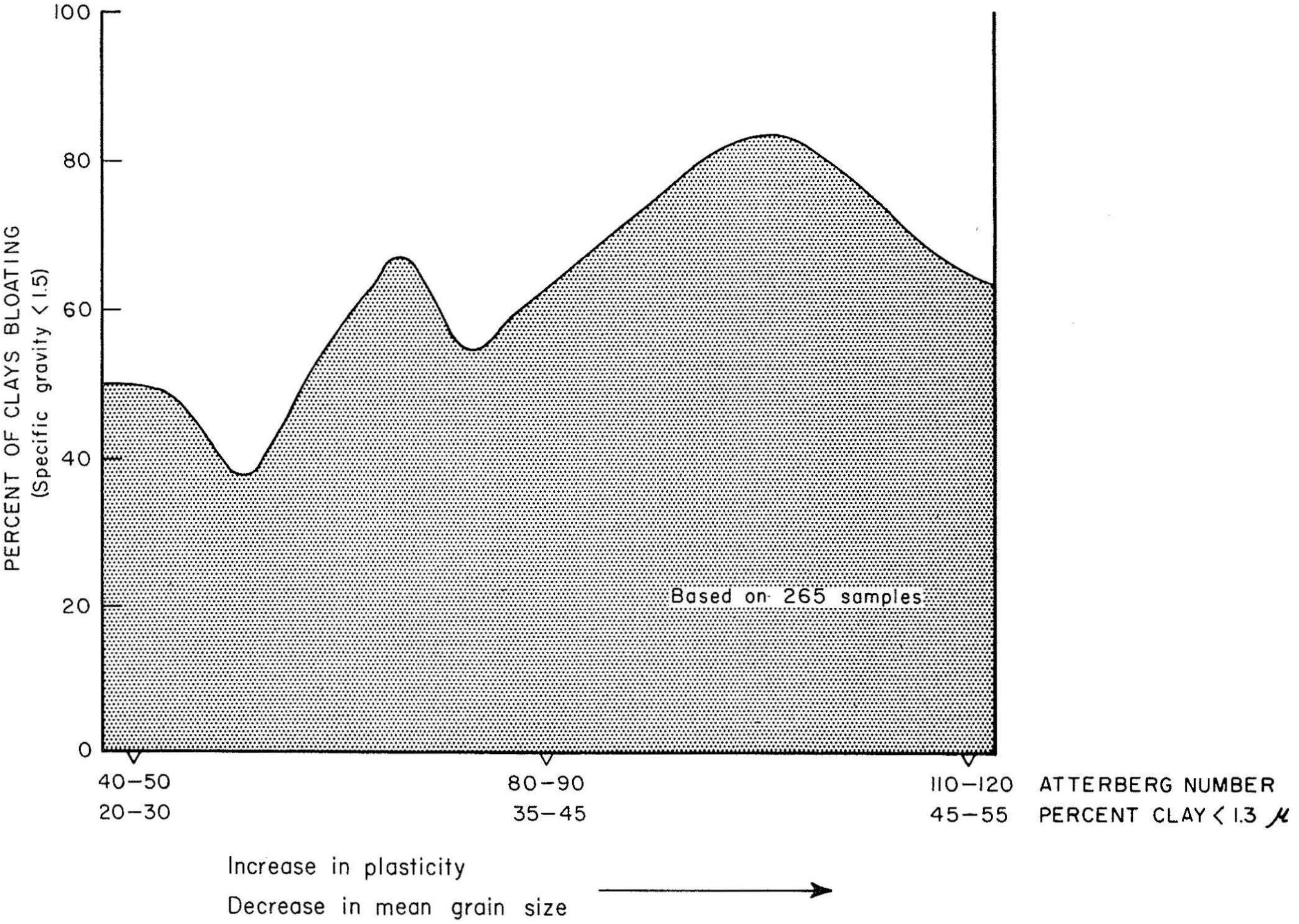


FIG. 9. Correlation of bloating incidence and clay texture.

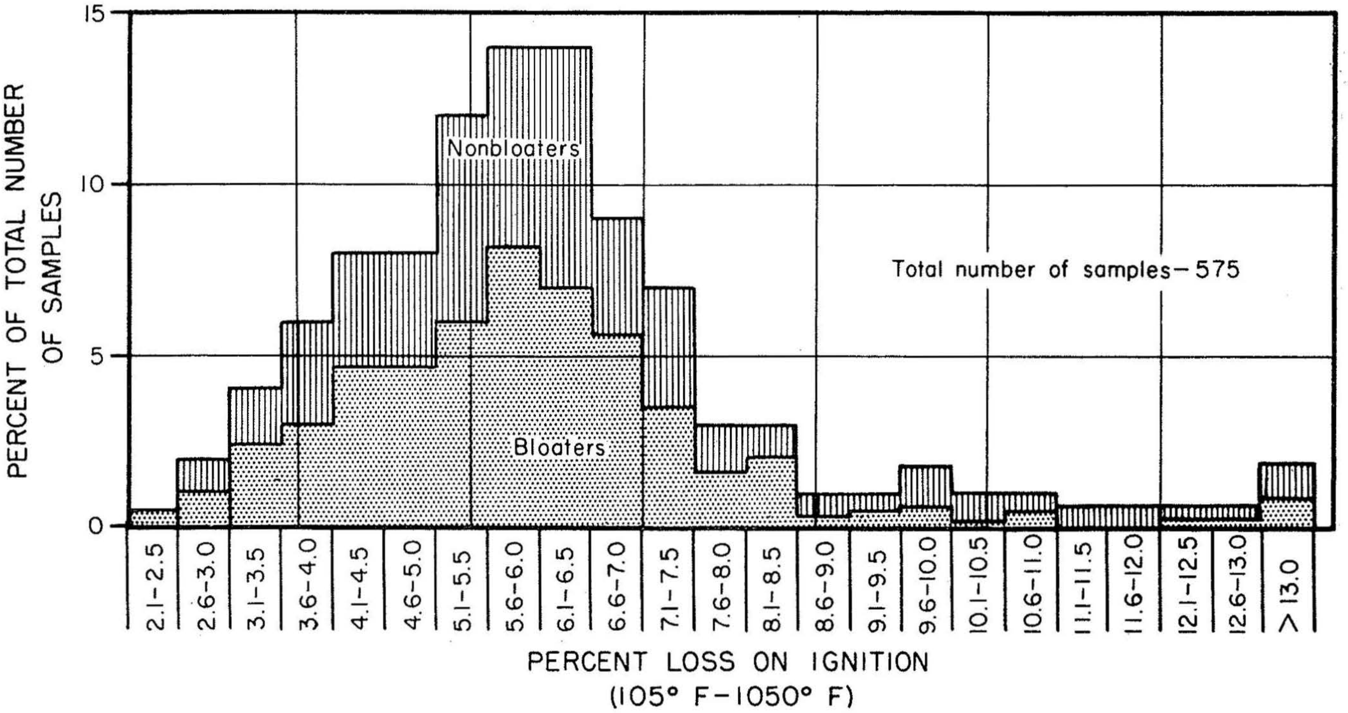


FIG. 10. Correlation of bloating incidence and loss on ignition.

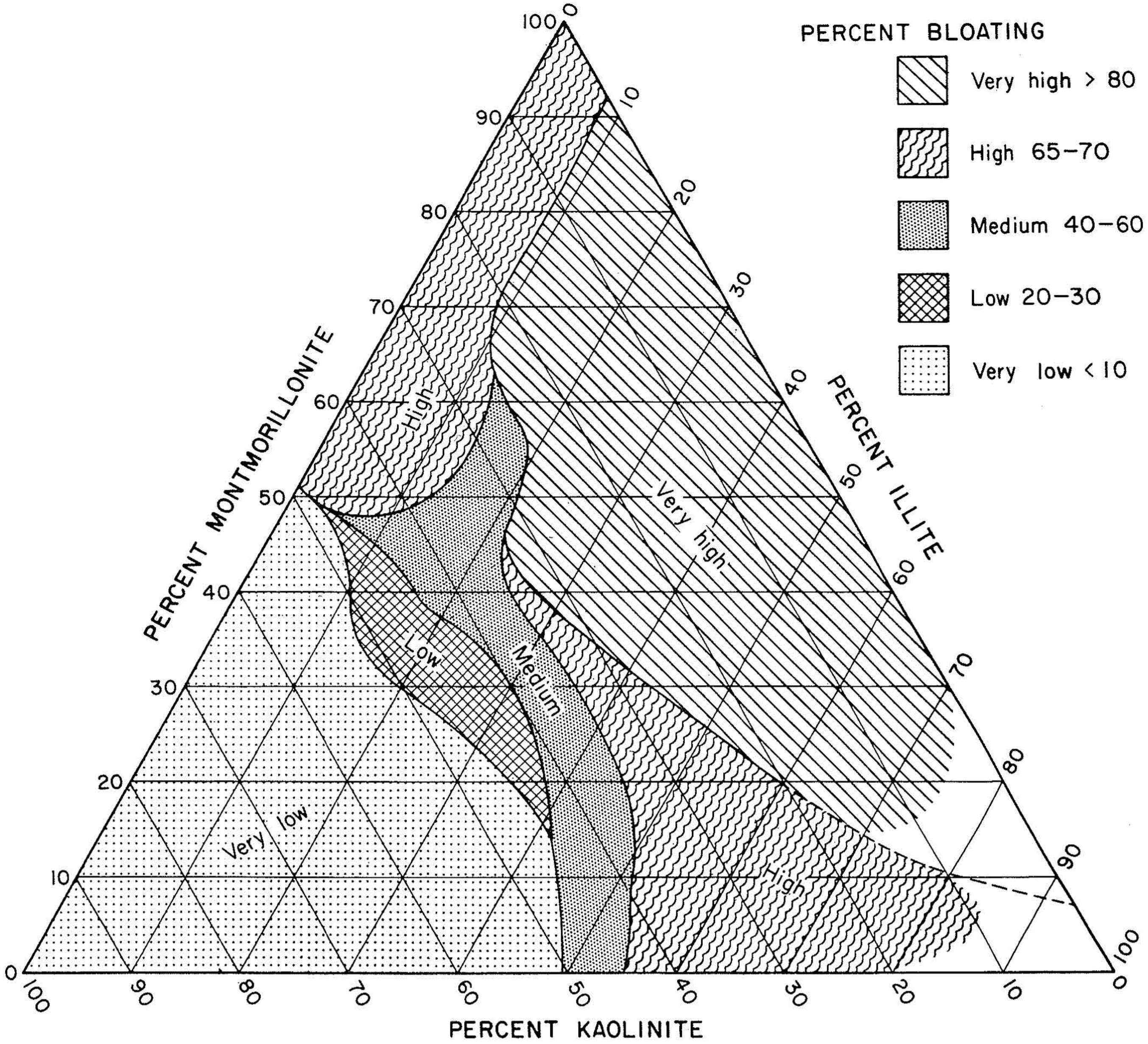


FIG. 11. Fields of bloating incidence based on clay mineral composition.

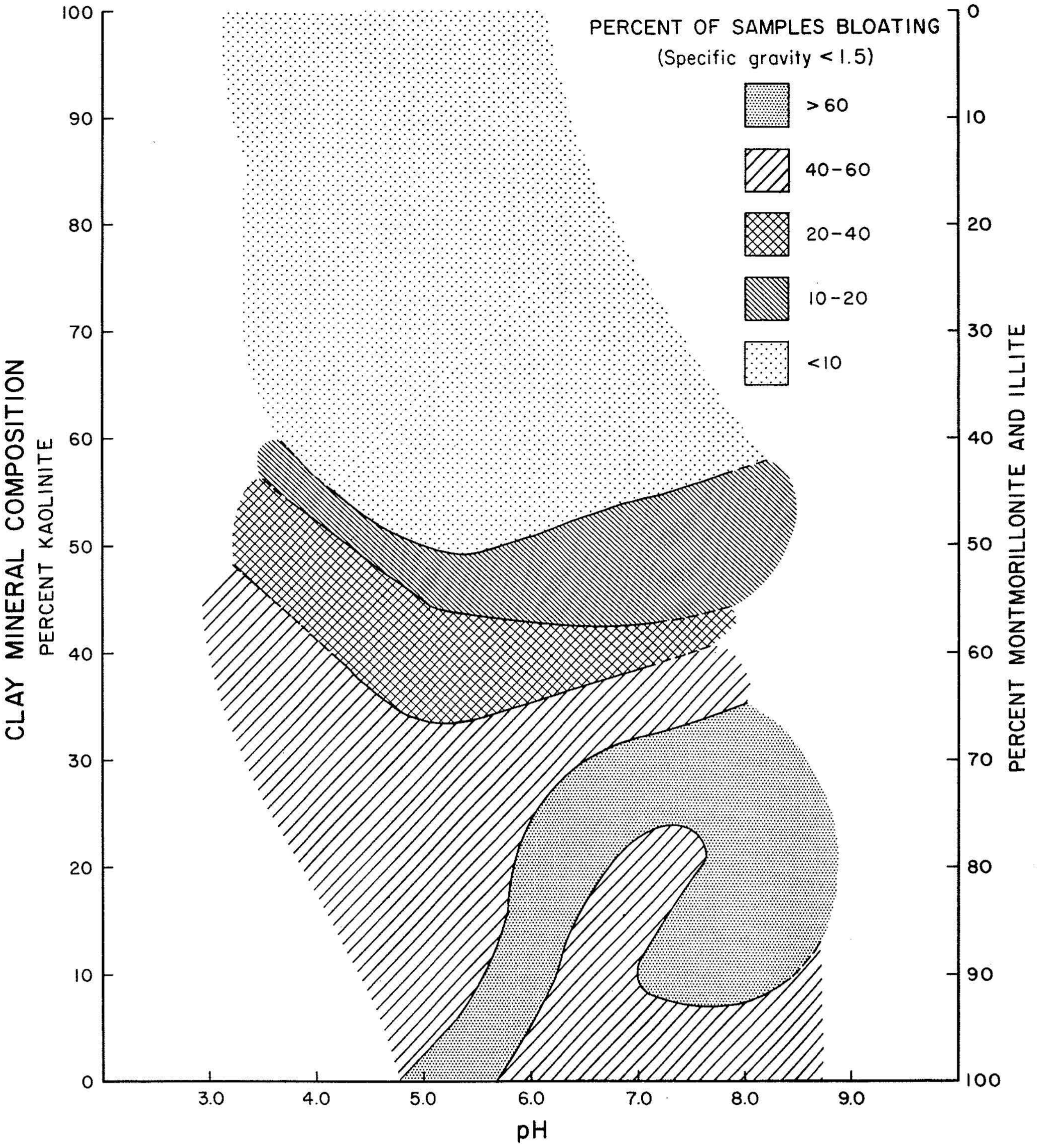


FIG. 12. Fields of bloating incidence based on clay mineral composition and pH.