Glaze Chemistry

Health risks associated with raw minerals and chemicals.

Most of the materials we use in making up glazes have some health concerns connected with them. They mainly fall into two camps; one is inhalation hazard concerning the dust from silica, or silica containing materials (e.g. feldspars and clays) and ingestion hazard from eating the raw material or eating from dishes glazed with glazes containing high levels of lead, barium, copper, chromium, manganese, cobalt, zinc, nickel and vanadium. This later risk is dependant on the type of glaze, its fired temperature and amount of material used. The risk from silica dust is a long term cumulative one, so keeping the workshop clean by regularly washing down surfaces is recommended, this includes floors, walls, rafters and ledges where fine dust may settle.

What is a glaze?

In its simplest meaning any glass that covers a ceramic object can be called a glaze. The term is related to glass and shares many of that substances properties, the chief difference between a glass and a glaze is related to the use each is put to.
We use glaze for a variety of reasons, some of which are listed below;

- To create a food safe surface for domestic ware,
- To produce a wide range of colours,
- To texture the surface of the pot,
- To change the degree of shine,
- To improve the strength and durability of the pottery,
- To add a new level of artistic merit,
- To allow the pottery to be fired to a wide variety of temperatures and conditions.

Another, more exact definition of glaze is a substance that is chiefly composed of silica, melted with a balance of fluxes and stabilised with alumina. This definition is more useful for us as it begins to set out a framework for us to learn about glazes.

Why are there different glazes?

There are different glazes because the uses a glaze can be put to are varied and there are many materials that can be used to make glazes. The tally of minerals in the Earth's crust puts silica at the top of the list, which makes it easy for all potters to find their chief glaze ingredient. Many of the other ingredients used in glazes, like clay for instance, are also very plentiful.

What is in a glaze?

1. Flux
Is any ingredient that is used to help melt the glaze or to lower the temperature that the glaze will melt at.
2. Stabiliser
Is any ingredient that is used to extend the melting range of a glaze and to stiffen the melted glaze.
3. Glass former
Is the main ingredient of a glaze and the one that needs additional melting from the fluxes and stiffening from the stabilisers. Silica is the main glass former.
4. Opacifier
Makes the glaze more opaque by obstructing the light as it passes through, often used to make a white glaze.
5. Colourant
These ingredients add colour to the base glaze and are used in small amounts, they are usually metals in some form like copper.

Oxide

Means an atom of oxygen combined with an atom of another element in various ratios (for instance lime is a mixture of 1 atom of calcium and 1 atom of oxygen). Ceramics is a study of oxides as almost all our ingredients are oxides before and after fusion in the kiln.
Another point of possible confusion is that some materials have more than one name, when an element gains an atom of oxygen it also changes its name, for example calcium plus oxygen becomes lime. Some materials have scientific names, geological names, common names, old usage names etc... Again using calcium as the example, calcium carbonate is called whiting or calcite or limestone.
Below is a list of the common oxides used in glazes.

NAME	COMMON NAME	CATEGORY	ABBREVIATION
Silicon Dioxide	Silica	Glass Former	SiO_2
Aluminium Oxide	Alumina	Stabiliser	Al_2O_3
Boric Oxide		Glass Former, Stabiliser, Flux	B_2O_3
Barium Oxide	Baria	Flux	BaO
Calcium Oxide	Lime	Flux	CaO
Potassium Oxide	Potash	Flux	K_2O
Sodium Oxide	Soda	Flux	Na_2O
Lithium Oxide	Lithia	Flux	Li_2O
Magnesium Oxide	Magnesia	Flux	MgO
Lead Oxide	Litharge	Flux	PbO
Strontium Oxide		Flux	SrO
Zinc Oxide		Flux	ZnO_2
Stannous Oxide	Tin	Opacifier	SnO_2
Titanium Dioxide	Anatase	Opacifier	TiO_2
Zirconium Oxide	Zirconia	Opacifier	ZrO_2
Copper Oxide		Colorant	CuO
Copper Carbonate		Colorant	$CuCO_3$
Cobalt Oxide		Colorant	CoO
Cobalt Carbonate		Colorant	$CoCO_3$
Manganese Dioxide		Colorant	MnO_2
Iron Oxide (red)		Colorant	Fe_2O_3
Rutile		Colorant	TiO_2
Vanadium Pentoxide		Colorant	V_2O_5
Nickel Oxide		Colorant	NiO

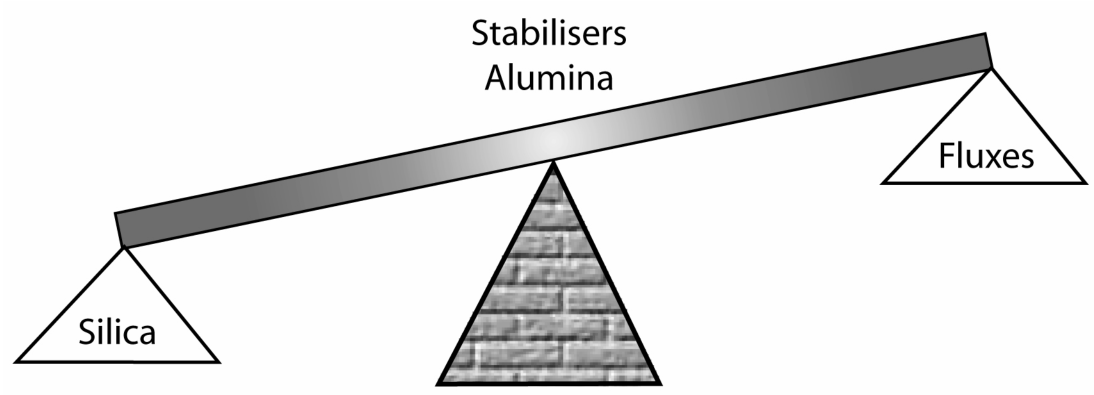
Most often materials used in glazes are not pure oxides, but rather combinations that nature has thrown together. These minerals are mined, refined, graded and then sold in bags to potters. You can also go out prospecting and locate some of these materials yourself, but a knowledge of what these rocks look like in their raw state and where to find them would require a reasonable level of geological awareness.
The list below gives you the more common minerals that we use in glaze making.

NAME	COMMON NAME	CATEGORY	ABBREVIATION
Silica	Flint, Quartz	Glass former	SiO_2
Orthoclase	Potash Feldspar	Complete glaze material	$K_2O.Al_2O_3.6SiO_2$
Albite	Soda Feldspar	Complete glaze material	$Na_2O.Al_2O_3.6SiO_2$
Lithium Feldspar	Petalite	Complete glaze material	$Li_2O.Al_2O_3.8SiO_2$
	Bone Ash	Flux, glass former	$Ca_3(PO4)_2$
Kaolin	China Clay	Stabiliser	$Al_2O_3.2SiO_2.2H_2O$
Calcite	Limestone, Whiting	Flux	$CaCO_3$
Colemanite	Gerstley Borate	Flux	$2CaO.3Ba_2O_3.5H_2O$
Dolomite		Flux	$CaMg(CO_3)_2$
Lead Bisilicate		Flux	$PbO.2SiO_2$
Lithium Carbonate		Flux	Li_2CO_3
Magnesium Carbonate		Flux	$MgCO_3$
Barium Carbonate		Flux	$BaCO_3$

Nepheline Syenite		Flux	$K_2O.3Na_2O.4Al_2O_3.8SiO_2$
Wollastonite		Flux	$CaSiO_2$
Talc		Flux	$3MgO.4SiO_2.H_2O$
Zinc Oxide	Zincite	Flux	ZnO_2

Balance

Now that we have a list of possible ingredients and a rough idea about their behaviour the next step is to combine them in certain ratios. This is where the idea of balance in a glaze comes from. On one side of the scales is the glass forming oxides and on the other side are the fluxes, in the middle are the stabilisers.



In practice the glass forming oxide is always Silica and Alumina is the major stabiliser used. So the real work of glaze making is the use of various fluxes and their proportion in the final mix. As you can see from the above lists, if we could deal directly with oxides alone it would be a relatively easy job to make up a glaze. But few of our materials are so pure, and those that are have been heavily processed and are more expensive. So we have to use the more common materials at hand.

Where do we get a glaze recipe from?

Sources include books, magazines, the internet, workshops and, of course, fellow potters. However remember to check that the firing temperature of the glaze matches the firing temperature of your clay and kiln. Also start to analyse your glazes by using the above balance as a starting point. How much of the glaze is feldspar, silica or the other fluxes? This will help you compare glazes and discard glazes that fall too far out of your preferred range.

One habit to get into early on is to write everything down, even if it seems trivial now. A few months or years from now it will be hard to remember exactly what the glaze looked like. The notes at the very least should include the recipe, the temperature fired to and what the clay was. You can also just make up a glaze recipe and if you follow the methods of testing that we are covering a successful glaze should be possible at any temperature. As a general rule of thumb, when listing materials, we choose the most complex material first and work our way towards the simplest of materials. So a very common glaze recipe might start with Potash Feldspar, then list the clay, then the simple fluxes like Whiting and end with Silica.
e.g.: Leach's Limestone Glaze for Cone 8 (also known as the 4,3,2,1 glaze)

Potash Feldspar	40
China Clay	10
Whiting	20
Silica	30

Although the above example glaze recipe looks simple with only 4 materials used, in reality the oxides that will be present in the final glaze are as follows:

K_2O	.264	Al_2O_3	.406	SiO_2	3.7
CaO	.736				

9.1:1 Si:Al Ratio

The numbers mentioned above are derived from the glaze recipe in a mathematical process that reduces the materials to their constituent parts, making comparisons between glazes that may have widely different materials possible. The procedure is called the Seger formula, or Molecular Unity Formula. It is not hard to work out, but it is a lot easier with glaze calculation programmes on computers.

In many ways the art of glaze making is all about balances and ratios of ingredients. Much of the analysis of glazes is done by comparing the amounts of various oxides present in a glaze, both against each other and against known limits. The main ratios that inform us about a glaze are the silica:fluxes ratio, the alumina:silica ratio and the flux ratio.

Silica:Fluxes Ratio

This ratio is important because to make a glaze you need lots of silica, you also need to melt it with the fluxes. However, too much silica will mean that not all of it will be melted with the fluxes and often results in a matte surface. Too little silica and not enough glass has been made and again the surface will be matte. However, as a shiny glaze needs at least 60% silica and because it is an easy ingredient to source it is not a difficult ratio to correct.

Silica:Alumina Ratio

This ratio governs the degree of shine and how melted the glaze becomes. This ratio is expressed with the alumina part equalling 1. For instance a silica alumina ratio of 9:1 means 9 silica for every 1 alumina and also indicates that the glaze will probably be glossy. When the ratio is below 4:1 then the glaze will be matte.

Flux Ratio

It is in the balancing of the various fluxes that the real art of glaze making comes to the fore. With about 13 possible sources of fluxes a great many combinations are possible. As a general rule of thumb, the more fluxes in a glaze make it more stable and adaptable. So rather than using only one, aim for about three major fluxes. The fluxes can also be broken up into several camps:

Alkalis	Sources	Oxides	Molecular Weight
Soda	Soda Feldspar	$Na_2O.Al_2O_3.6SiO_2$	524.6
	Borax	$Na_2O.2B_2O_3.10H_2O$	
	Nepheline Syenite	$K_2O.3Na_2O.4Al_2O_3.8SiO_2$	1169
Potash	Potash Feldspar	$K_2O.Al_2O_3.6SiO_2$	556.8
Lithium	Petalite	$Li_2O.Al_2O_3.8SiO_2$	612.6
	Spodumene	$Li_2O.Al_2O_3.4SiO_2$	
	Lithium Carbonate	Li_2CO_3	73.8

General qualities common to the group: early melting, high shrinkage, bright colour response, soft and easily worn, good in oxidation or reduction, use less for high temperatures.

Alkaline Earths	Sources	Oxides	Molecular Weight
Lime	Whiting	$CaCO_3$	100.1
	Wollastonite	$CaSiO_2$	116.2
	Dolomite	$CaMg(CO_3)_2$	
Magnesia	Magnesium Carbonate	$MgCO_3$	84.3
	Talc	$3MgO.4SiO_2.H_2O$	379.3
	Dolomite	$CaMg(CO_3)_2$	184.4
Baria	Barium Carbonate	$BaCO_3$	197.3
Strontium	Strontium Carbonate	$SrCO_3$	

General qualities common to the group: active mainly at high temperatures, average shrinkage, not much influence on colour unless in large amounts, hard and strong glazes, good in oxidation or reduction, use more for high temperatures.

The other fluxes are quite individual and are:

Zinc Oxide		ZnO_2	81.4

General qualities: good as a supplementary flux, active from mid to high temperatures, small amounts help glaze fit and colour response, only used in oxidation.

Lead Oxide	Red Lead (TOXIC)	PbO	
	Lead Monosilicate	$PbO.SiO_2$	
	Lead Bisilicate	$PbO.2SiO_2$	343.4

General qualities: very useful low temperature flux, can be toxic in fired form if incorrectly used, low shrinkage, good colour response, only used in oxidation, soft and easily worn.

Boric Oxide	Borax	$Na_2O.2B_2O_3.10H_2O$	
	Standard Borax Frit	$Na_2O.2B_2O_3.3SiO_2$	
	Colemanite	$2CaO.3B_2O_3.5H_2O$	411

I'm including the following ingredients to complete the list of materials and their weights

China Clay		$Al_2O_3.2SiO_2.2H_2O$	258.2
Silica		SiO_2	60.1

General qualities: a complex material, boric oxide can act like a flux, or stabiliser or glass former, generally used as a very early melting flux, useful over the whole range of temperatures, low shrinkage, good colour response, used mainly in frit form, good in both oxidation or reduction.

At this stage I should mention why I haven't talked about colour. That is because the colouring oxides are usually added in small percentages and have very little effect on the glaze other than colour. So it is important to first come up with a base glaze that exhibits the qualities you want to see from a glaze, like the degree of shine or opacity.

These notes are very much a general introduction to the world of glaze chemistry. In summary the most important things to learn are your materials – what's in them, how do they react in the kiln and then you will gain confidence in combining them in glazes. Also keep in mind this idea of balance and ratios so that if a new glaze comes your way you can start to guess its likely effects even before you fire up a test. Which brings me to the final point - remember to label and note down everything!