Investigation of Concrete Aggregate for Alkali-Carbonate Reaction

AAR Reactions

AAR Reactions are chemical reactions between the cement and the aggregate causing the concrete to deteriorate.

There are two AAR reactions based on the reactive mineral type:

- **Alkali-Silica Reaction (ASR) with unstable forms of silica (most common)**
- **Alkali-Carbonate Reaction (ACR) with certain dolomite textures (least common)**

Both are destructive, are not mutually exclusive, and under the right conditions cyclic.

This presentation is focusing on ACR.

Why investigate for a "uncommon" reaction?

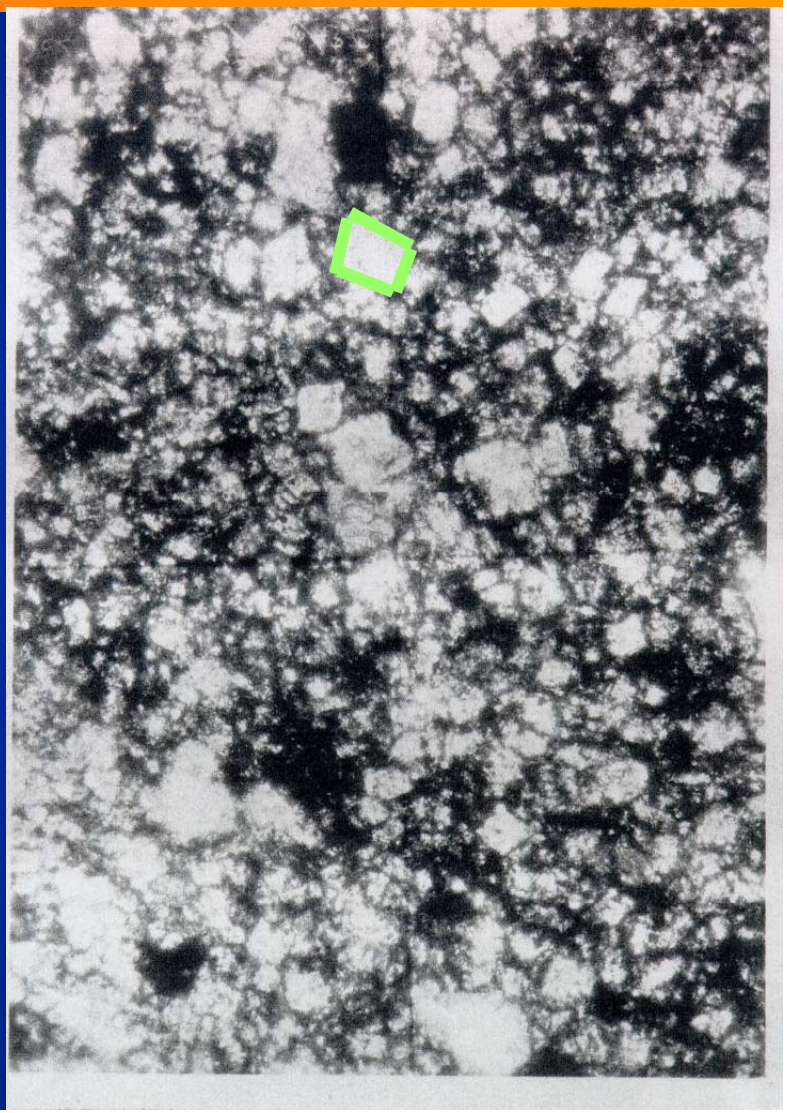
- ACR cannot be mitigated for. The addition of fly ash, GGBFS, or silica fume do nothing to stop the reaction.
- It requires only a little alkali to start the reaction
- Once the reaction is started, it does not stop until all aggregates have reacted destroying the concrete.
- It is the hardest reaction to identify when investigating an affected structure because its byproduct, brucite is very difficult to find even by microscopic examination. It does not have clear cut evidence like ASR.
- If reactive minerals for both ASR and ACR are present, both reactions are occurring and eventually the presence of the silica gel will obscure any evidence of ACR.

Chickamauga Lock

1937-39-Spillway deck poured
1941-Lock and Dam completed
1946-Cracking is a problem
1963 petrographic-no silica gel or brucite found
1970 petrographic-"AAR reaction definitely occurring", no byproduct
1993-94 petrographics-positive identification of silica gel
1996 petrographic-silica gel and brucite identified
1997 petrographics-only found silica gel

Chickamauga Petrographics

- Review of the 1930's petrographic examination of the aggregate showed 4-25% chert AND 5-32% dolomite rhombs with 10-41%insoluble residue matrix. The right mineral compositions for both ASR AND ACR.
- From the lack of by product for the first 25 years of expansion, it is logical to assume the ACR started first.



Definition

The Alkali-Carbonate Reaction is a chemical reaction between hydroxyl ions associated with the alkalis sodium and potassium in the cement and certain dolomitic textures in the aggregate resulting in expansion and eventually cracking of the hardened concrete.

Conditions Required for ACR

Alkali Content in the concrete

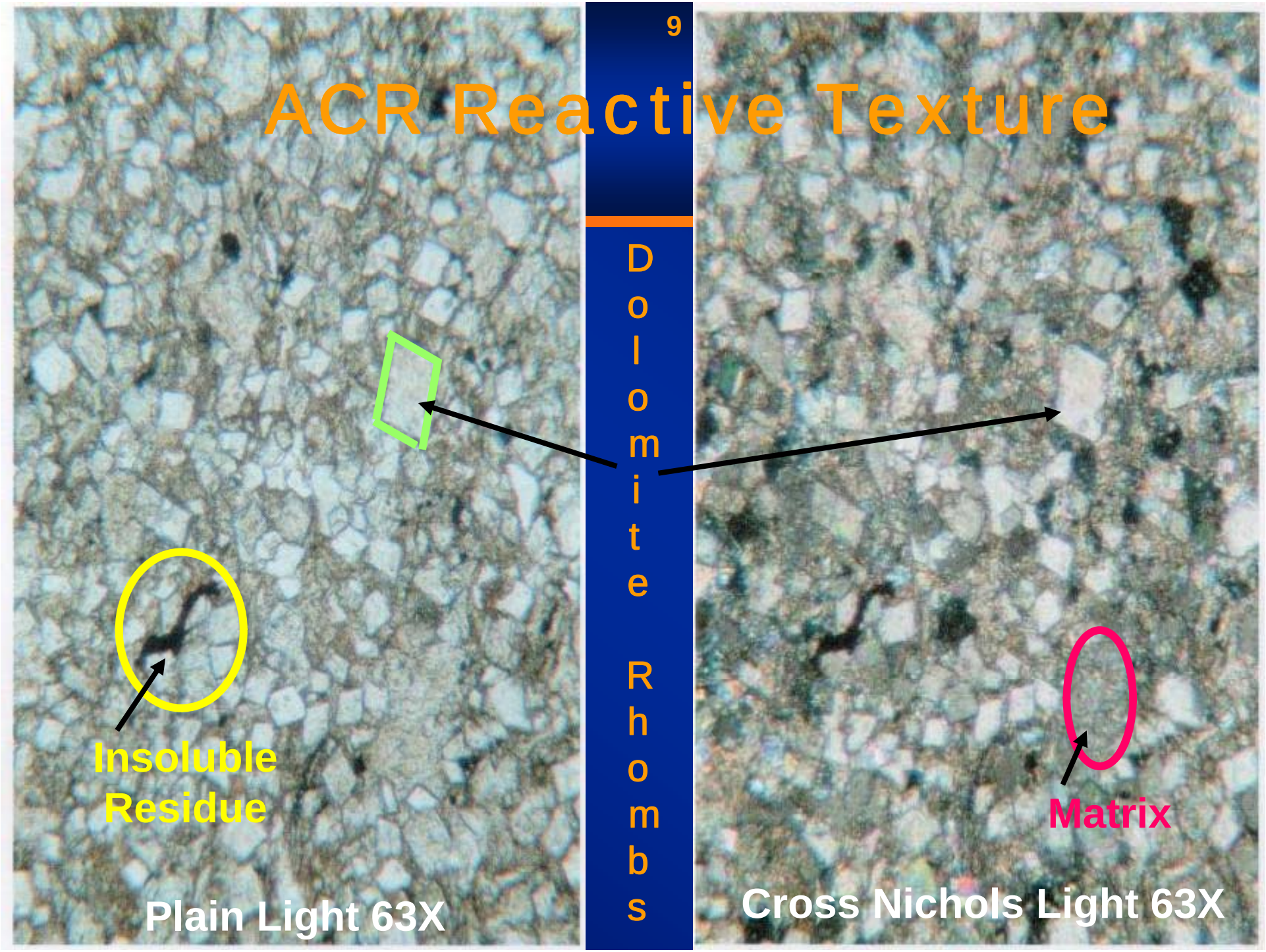
- The industry limit for Equivalent Alkalies in cement is 0.6% which is NOT low enough to stop ACR. Research has indicated the cement alkali content would need to be lower than 0.4% and still be combined with other preventative measures to suppress the reaction.
- Alkalis may come from other sources than just cement such as cementitious materials, aggregates (feldspars), local water, soil, or deicing agents (Potassium Acetate).
- A free alkali content of 2.0 kg/m^3 or 0.12 lbs/ft^3 in the concrete is normally sufficient to allow a reaction.
- ACR is a cyclic reaction, which means once it starts it can generate it's own (Na, K, Li) OH to continue the reaction.

Reactive Aggregate

Dolomite / Dolomitic Limestone –

- **10 to 85% dolomite and 5-50% insoluble residue.**
- **Specifically dolomite rhombohedra crystals in a fine grained matrix of calcite and insoluble residue (clay and silica).**
- **A pore structure that allows alkali solution to penetrate the rock**

ACR Reactive Texture



ACR Reaction

1) $CaMgCO_3 + 2(Na,K)OH \rightarrow Mg(OH)_2 + CaCO_3 + (Na,K)_2CO_3$

Dolomite + Alkali Hydroxide → Brucite + Calcite + Alkali Carbonate

2) $(Na,K)_2CO_3 + Ca(OH)_2 \rightarrow 2(Na,K)OH + CaCO_3$

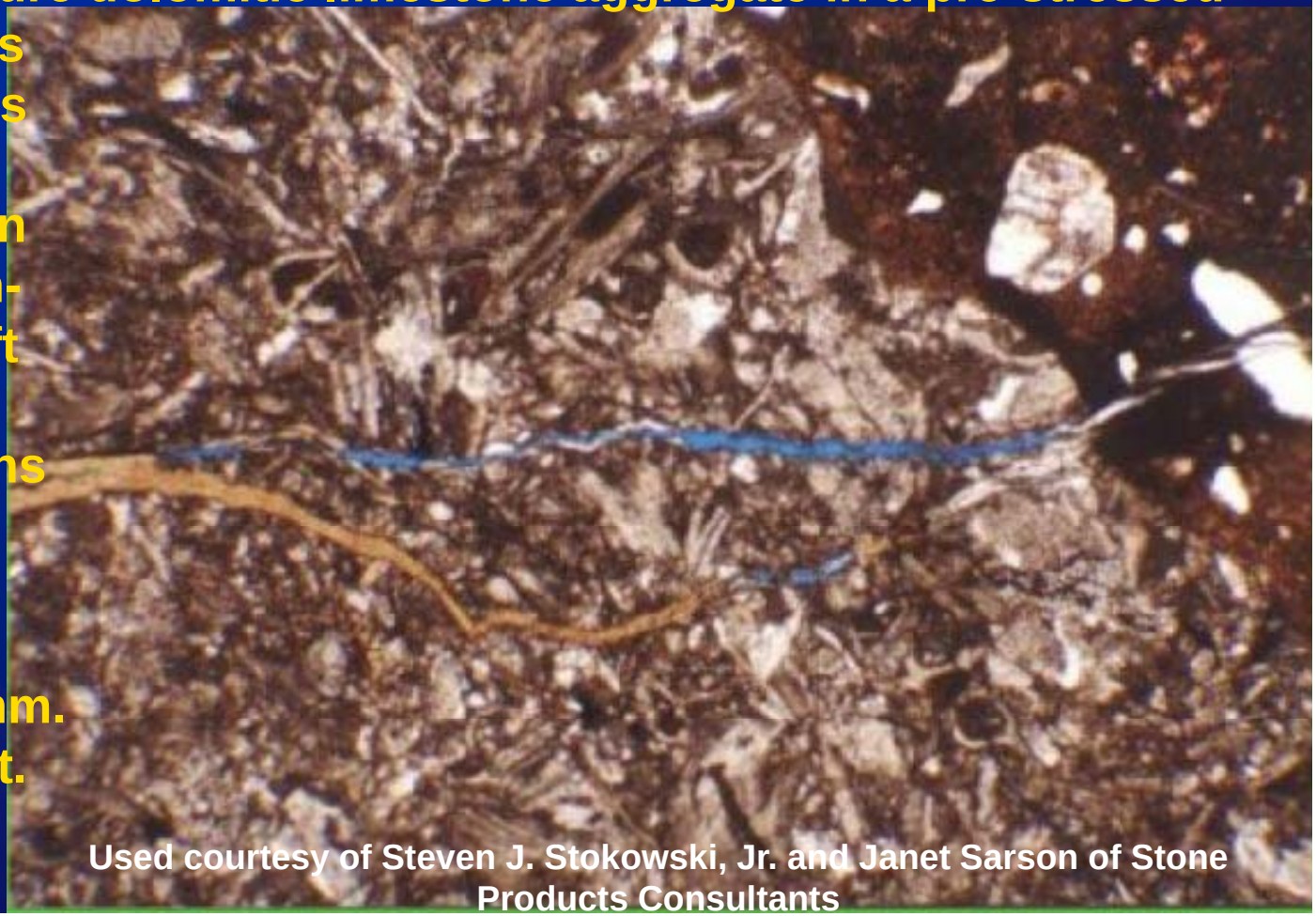
Alkali Carbonate + Cement Hydration (Portlandite) → Alkali Hydroxide + Calcite

3) Repeat first reaction

LiOH also causes expansion but not at the rate that NaOH and KOH does.

Brucite

Photomicrograph of crack, partially filled with brucite, from ACR deterioration of impure dolomitic limestone aggregate in a pre-stressed concrete. Crack runs through fossiliferous carbonate particle into cement paste on right. The brownish-yellow deposit in left side of crack is brucite. Blue sections of crack are filled with blue epoxy for clarity. Field width approximately 4.8 mm. Plane polarized light.



Used courtesy of Steven J. Stokowski, Jr. and Janet Sarson of Stone Products Consultants

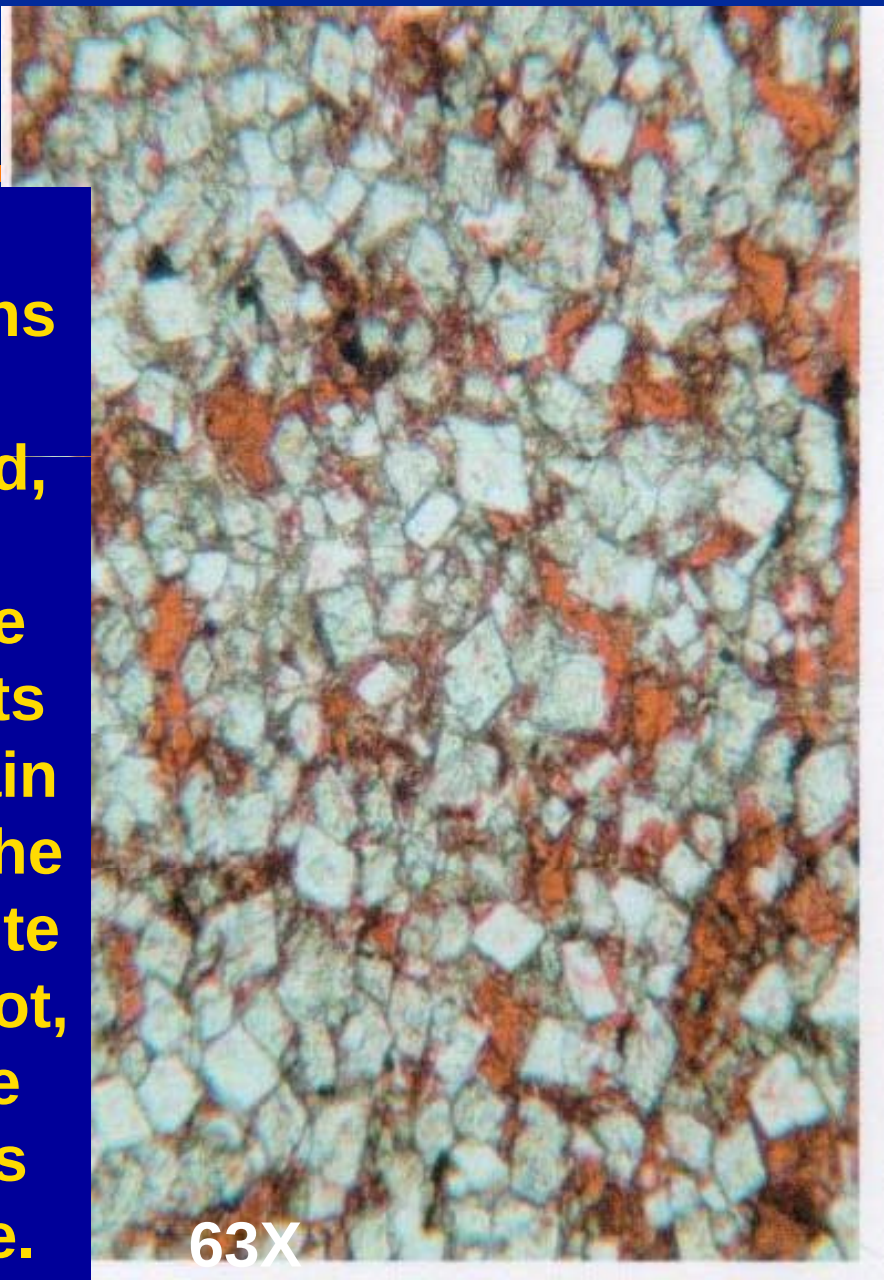
Early vs. Late Expanders

- **Early Expanders - dolomite rhombohedra crystals floating in a fine grained matrix of calcite and insoluble residue (clay and silica). The calcite to dolomite ratio is approximately 1 to 1 with 5 to 25% insoluble residue. The reaction usually shows expansion with in the first 5 years of the project.**

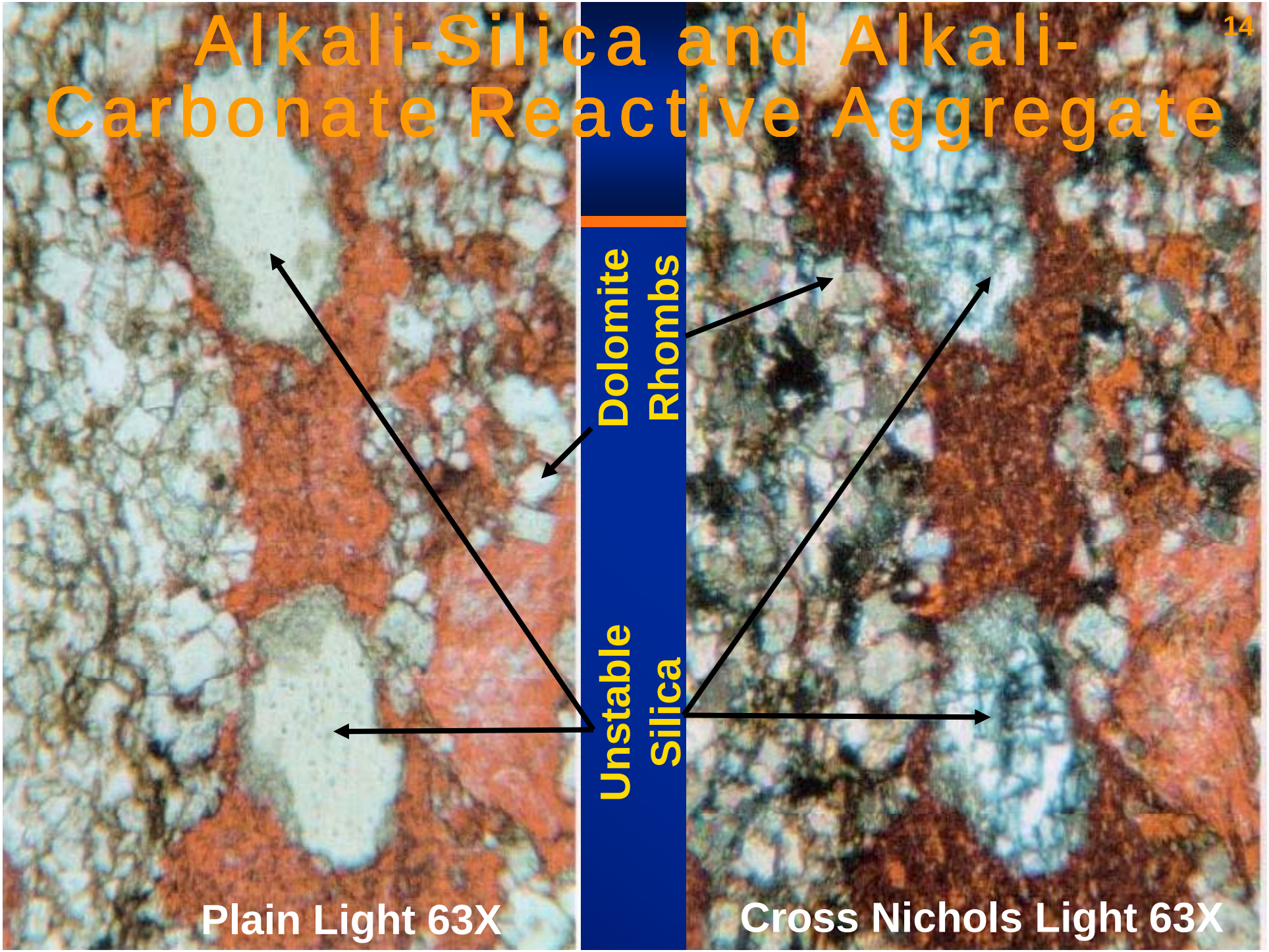
- **Late Expanders – has more or larger dolomite crystals so the crystals interlock, decreasing the calcite/clay/silica matrix and slowing down the reaction. Matrix also is not as fine grained as in the Early Expanders. The dolomite content is 75 to >90% of the soluble content and the rock contains 10 to 25% calcite and 21 to 49% insoluble material. The Calcite:Dolomite ratio is between 0.14:1 and 0.36:1. These can take 10 to 20 years before expansion shows in the project.**

Potential Early vs. Later Expander

Thin sections were stained, the calcite accepts the stain while the dolomite does not, so the pink is calcite.



Alkali-Silica and Alkali-Carbonate Reactive Aggregate



Late Expanders

- It is much more difficult to distinguish between Late Expanders and non-reactive Dolomite rocks. There has even been some dolomite rock with no limestone and very little clay/silica that have expanded.
- All occurrences of carbonate rock that have been found to be reactive have portions of the dolomite rhomb texture. However, not all dolomitic limestones with this texture expand with sufficient force to cause distress.
- There have been many structures built out of good dolomite aggregate.

Determining if your aggregate is potentially reactive

Sampling the aggregate

- Procure a good map of the quarry to be able to judge the overall quality of the quarry and determine is selective quarrying is required.
- Best if possible to test a core or cores from the quarry. Ledge rocks are difficult to collect and to ensure full coverage of the quarry.
- Take the petrographic samples and the samples for the ASTM C 586 tests from the same sample/location. This way there is good correlation between the two tests.

ACR Tests

- 1) ASTM C 295 Petrographic Examination
- 2) ASTM C 586 Potential Alkali Reactivity of Carbonate Rocks for Concrete Aggregate (Rock Cylinder Method)
- 3) ASTM C 1105 Length Change of Concrete Due to Alkali-Carbonate Rock Reaction

ACR Tests on Cores or Ledge Rocks

- **ASTM C 295 Petrographic – determines the amount of reactive minerals and textures in aggregate.**
- **ASTM C 586 Potential Alkali Reactivity of Carbonate Rocks – a 11/32 inch diameter by 1-3/8 inch long rock cylinder is cored out of the ledge rock and soaked in NaOH at room temperature for 1-12 months.**

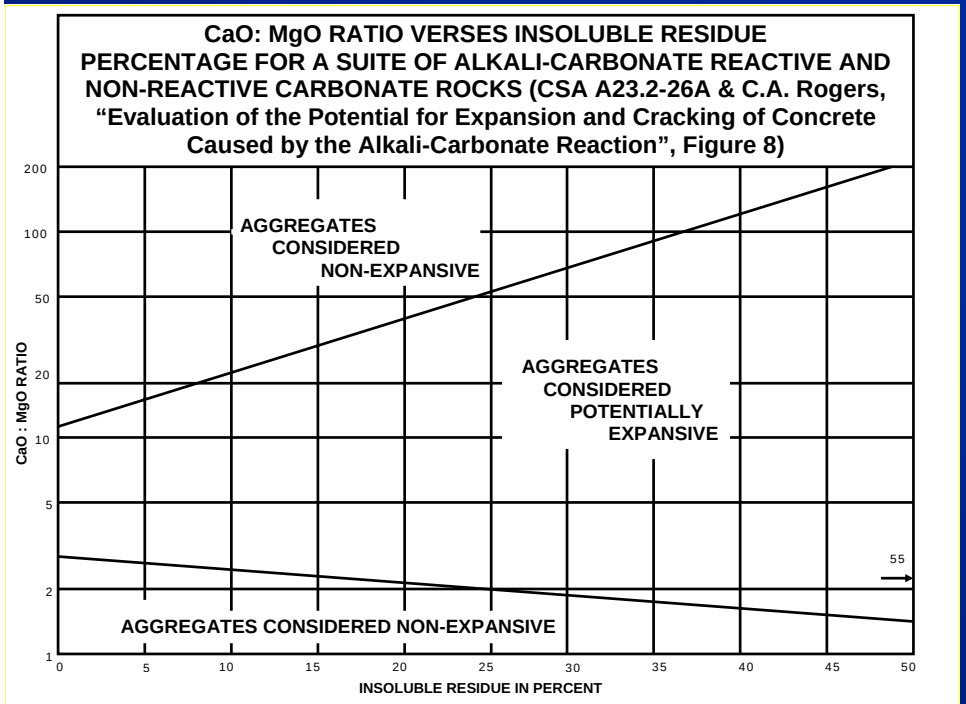
Petrographic Test

- 1) X-ray diffraction will determine amount of dolomite, calcite, and insoluble reside in the sample but cannot determine the type or texture.
- 2) Microscopic Thin Sections (25-30µm) will determine type and texture of the dolomite, calcite, and insoluble residue in the aggregate.
- 3) Ultra-Thin Thin-Sections (10-15 µm) to accurately discern the reactive texture since most of the dolomite rhombs are 25µm or less.

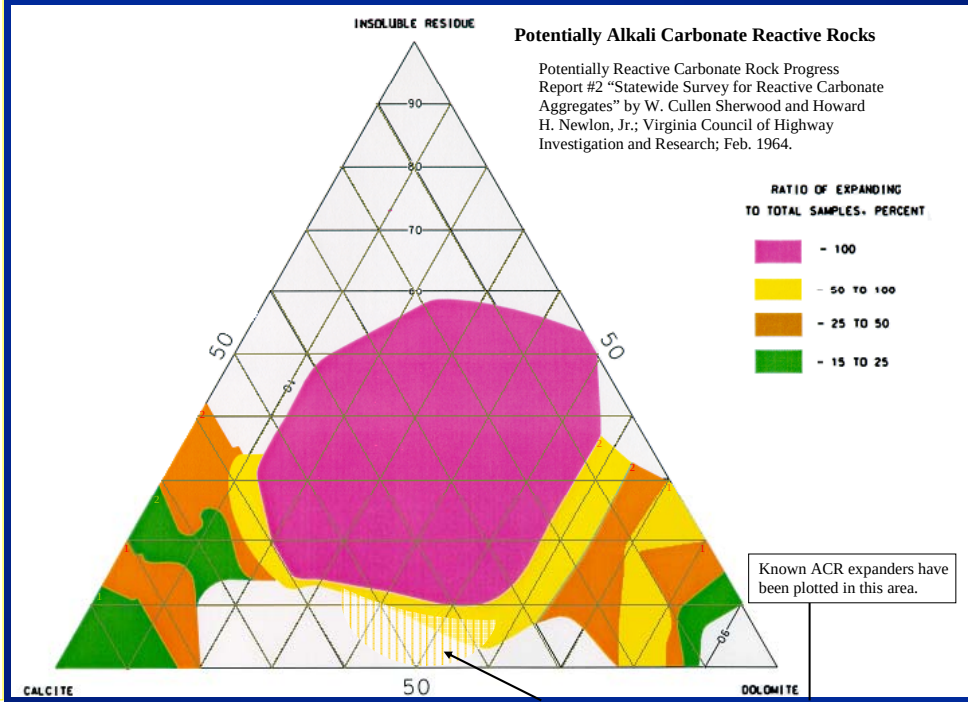
ACR Petrographic Prediction Diagrams

- **2 diagrams use chemical composition of the rock to predict potential ACR expansion.**

Canadian Standards Association CSA A23.2-26A



Virginia Council of Highway Investigation and Research

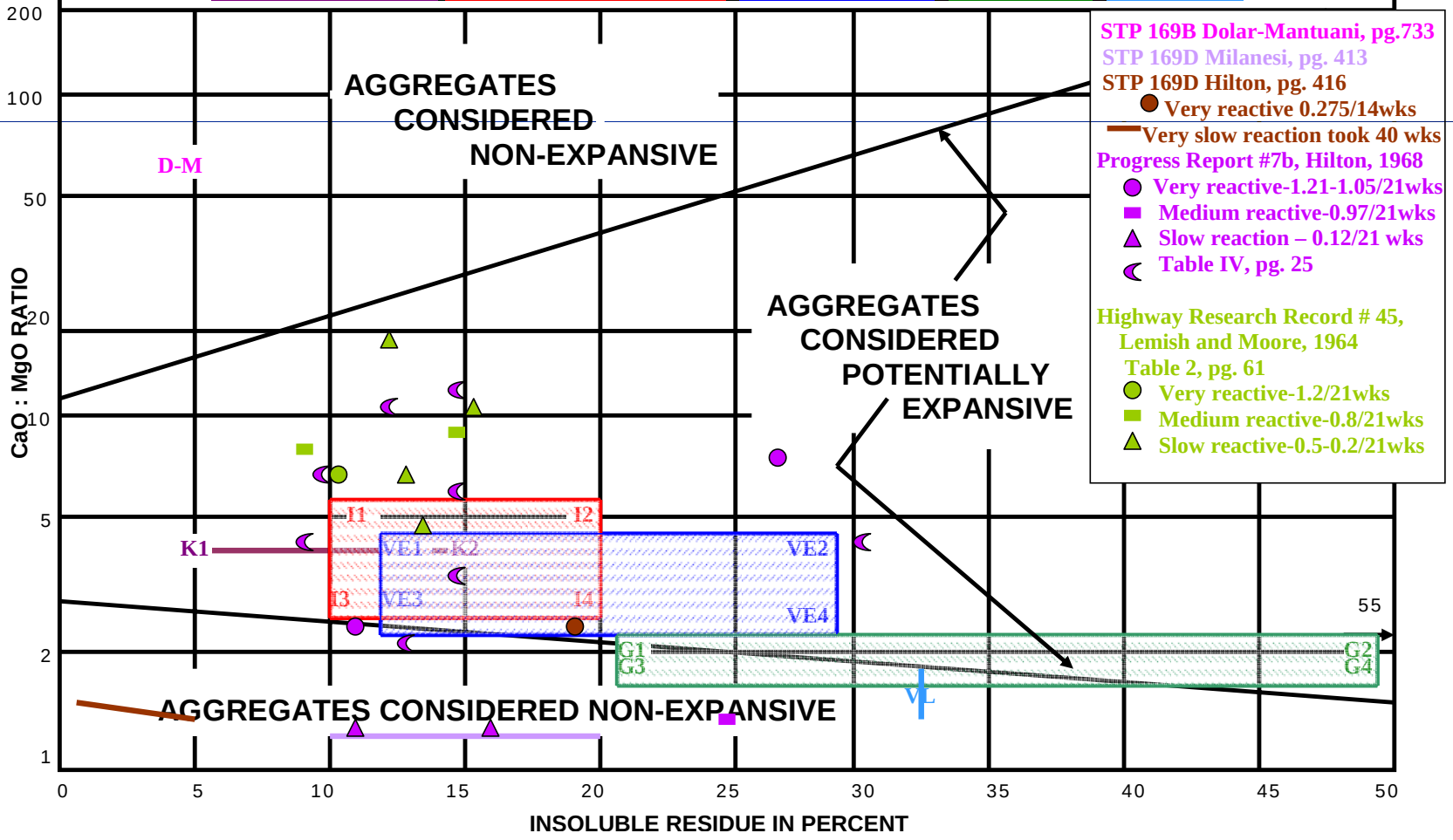


Known ACR Expanders

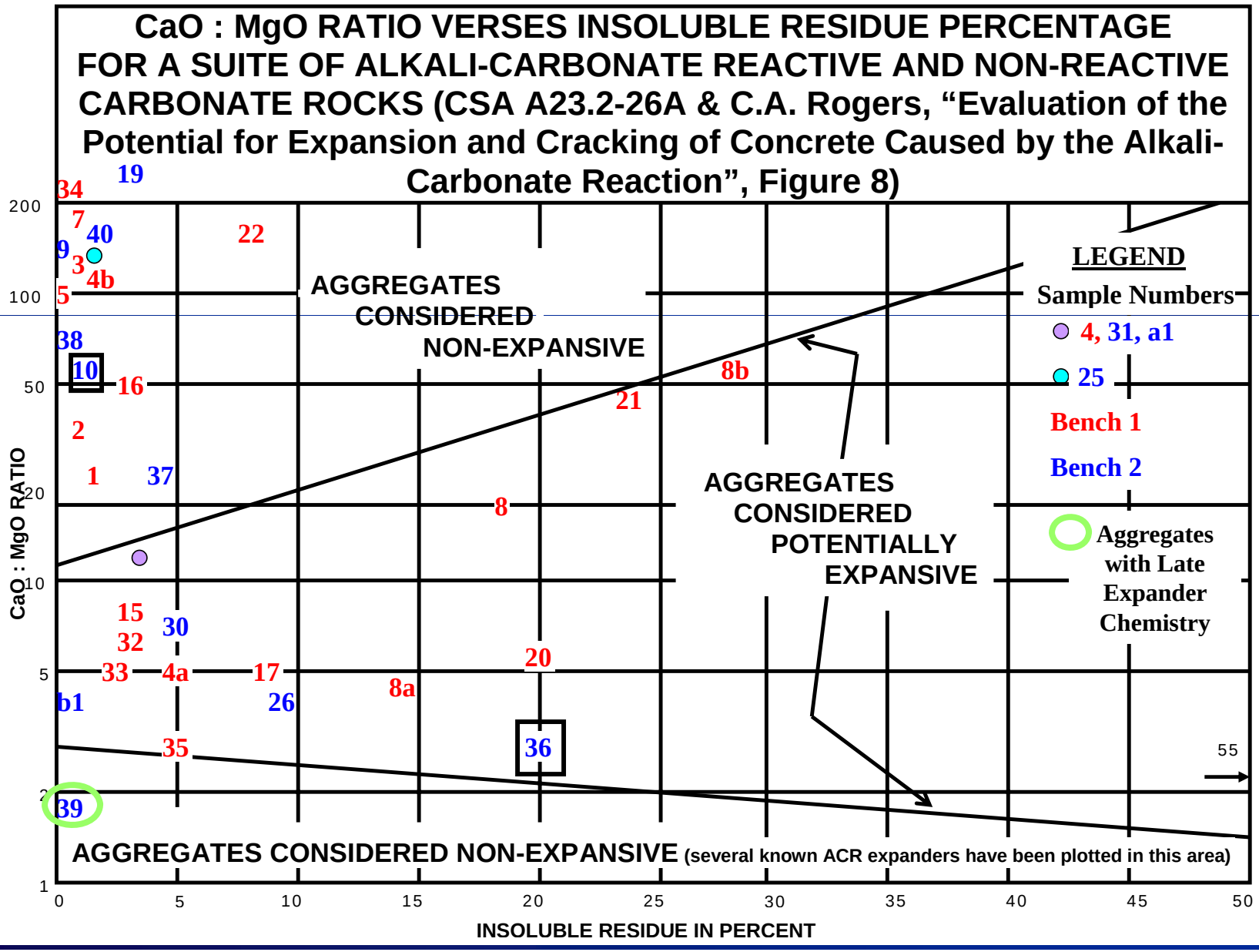
CaO:MgO RATIO VERSES INSOLUBLE RESIDUE PERCENTAGE FOR A SUITE OF ALKALI-CARBONATE REACTIVE AND NON-REACTIVE CARBONATE ROCKS (CSA A23.2-26A & C.A. Rogers, "Evaluation of the Potential for Expansion and Cracking of Concrete Caused by the Alkali-Carbonate Reaction", Figure 8)

Known Alkali-Carbonate Reactors – ASTM STP 169D-pg. 414, Table 1

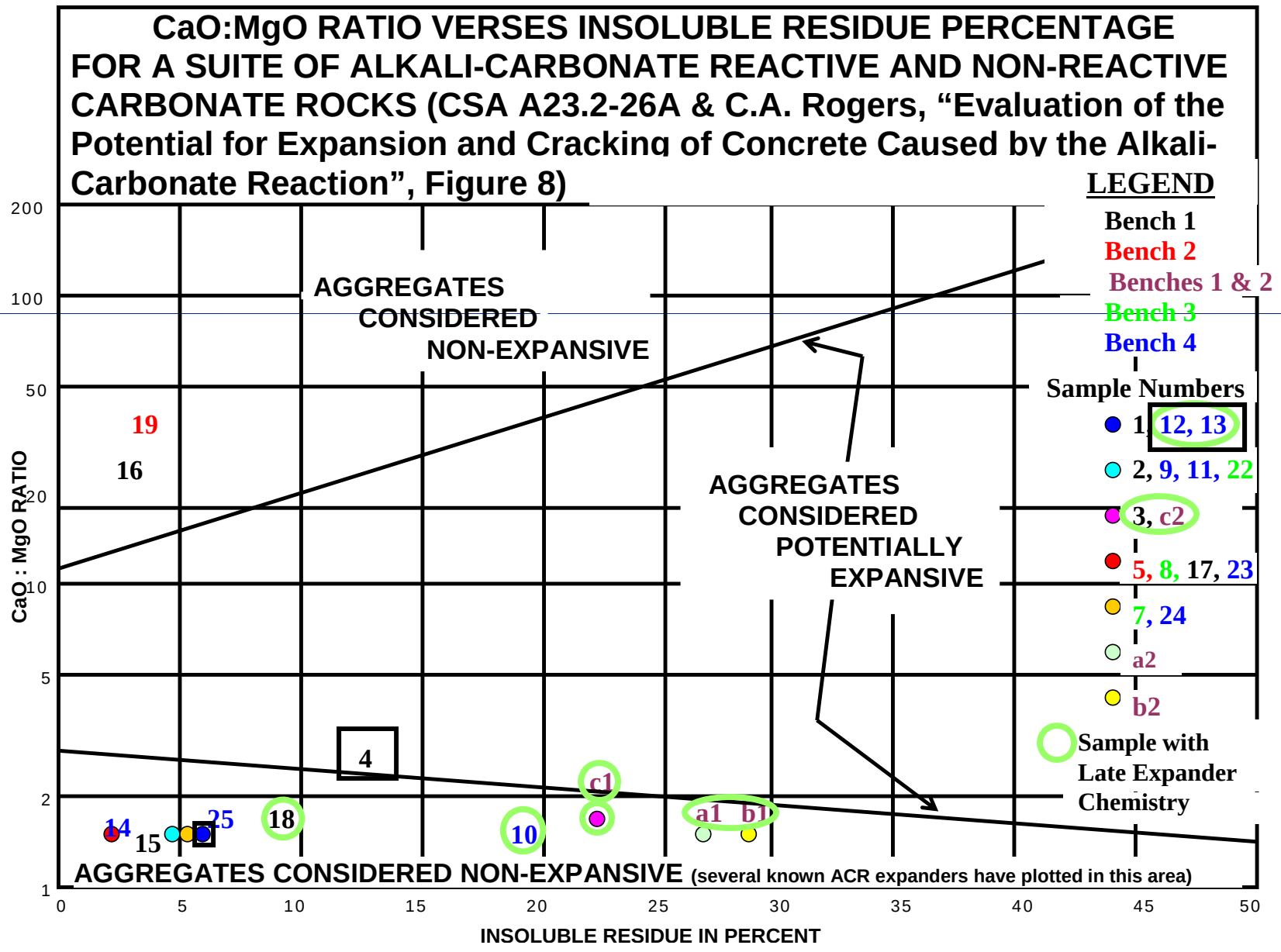
K - Kingston, Ontario; I - Iowa, Illinois, & Indiana; VE - Virginia-Early; G - Gull River; Virginia-Late



Limestone Quarry



Dolomite Quarry



Known ACR Expander

Known Alkali-Carbonate Reactors – ASTM STP 169D – pg. 414, Table 1

- Kingston, Ontario – Early Expander
- Iowa, Illinois, & Indiana – Early Expander
- Virginia – Early Expander
- Gull River Ontario – Late Expander
- Virginia – Later Expander
- STP 169B Dolar-Manuani, pg. 733
- STP 169D Milanesi's Expander – pg. 413

STP 169D Hilton pg. 416

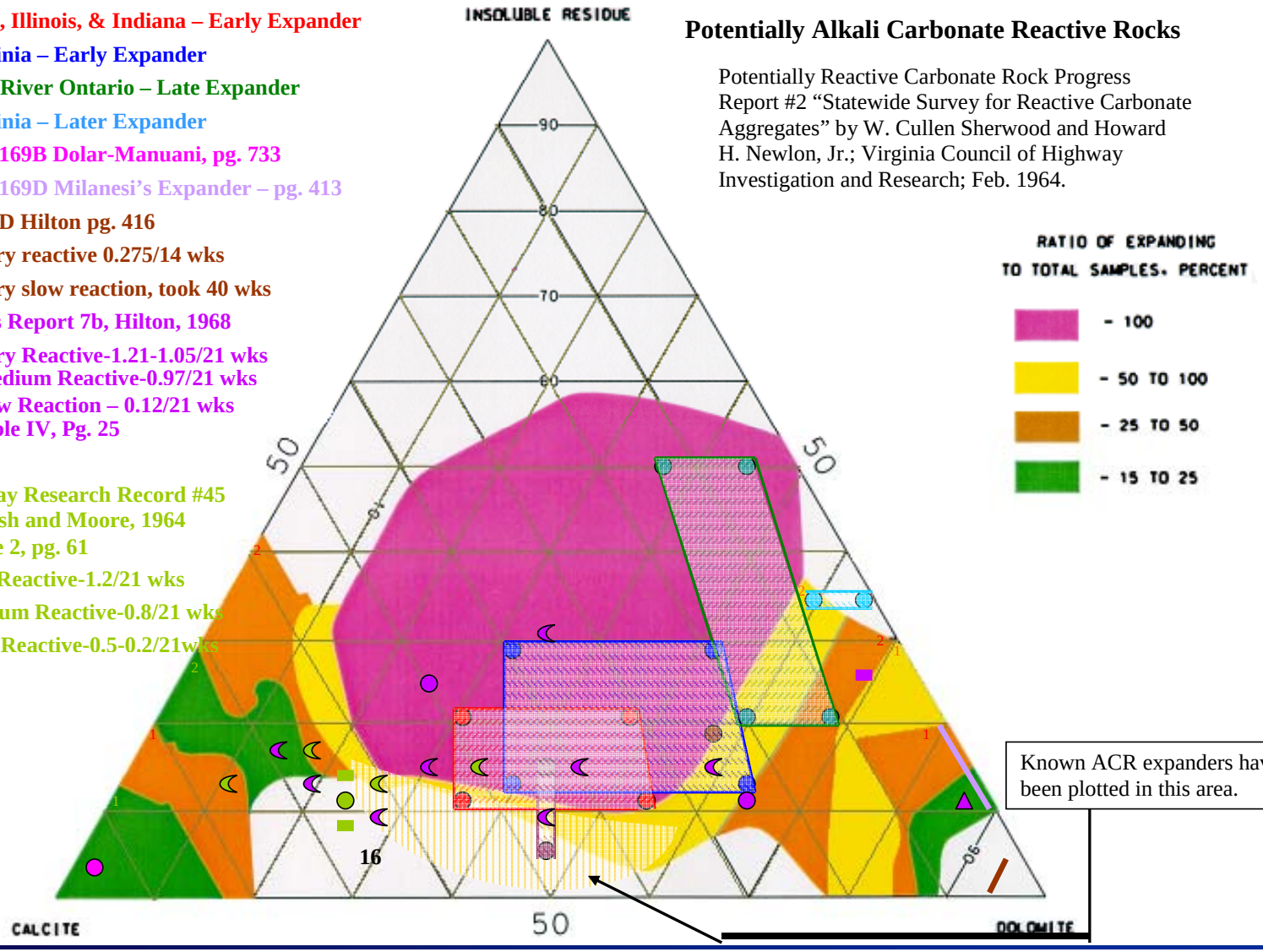
- Very reactive 0.275/14 wks
- Very slow reaction, took 40 wks

Progress Report 7b, Hilton, 1968

- Very Reactive-1.21-1.05/21 wks
- Medium Reactive-0.97/21 wks
- Slow Reaction – 0.12/21 wks
- Table IV, Pg. 25

Highway Research Record #45
Lemish and Moore, 1964
Table 2, pg. 61

- Very Reactive-1.2/21 wks
- Medium Reactive-0.8/21 wks
- Slow Reactive-0.5-0.2/21wks



Potentially Alkali Carbonate Reactive Rocks

Potentially Reactive Carbonate Rock Progress Report #2 "Statewide Survey for Reactive Carbonate Aggregates" by W. Cullen Sherwood and Howard H. Newlon, Jr.; Virginia Council of Highway Investigation and Research; Feb. 1964.

Known ACR expanders have been plotted in this area.

Limestone Quarry

 # - core sample number that has potential for expansion or plots differently than the majority of passing samples

○ core sample that does not exceed limit of expansion

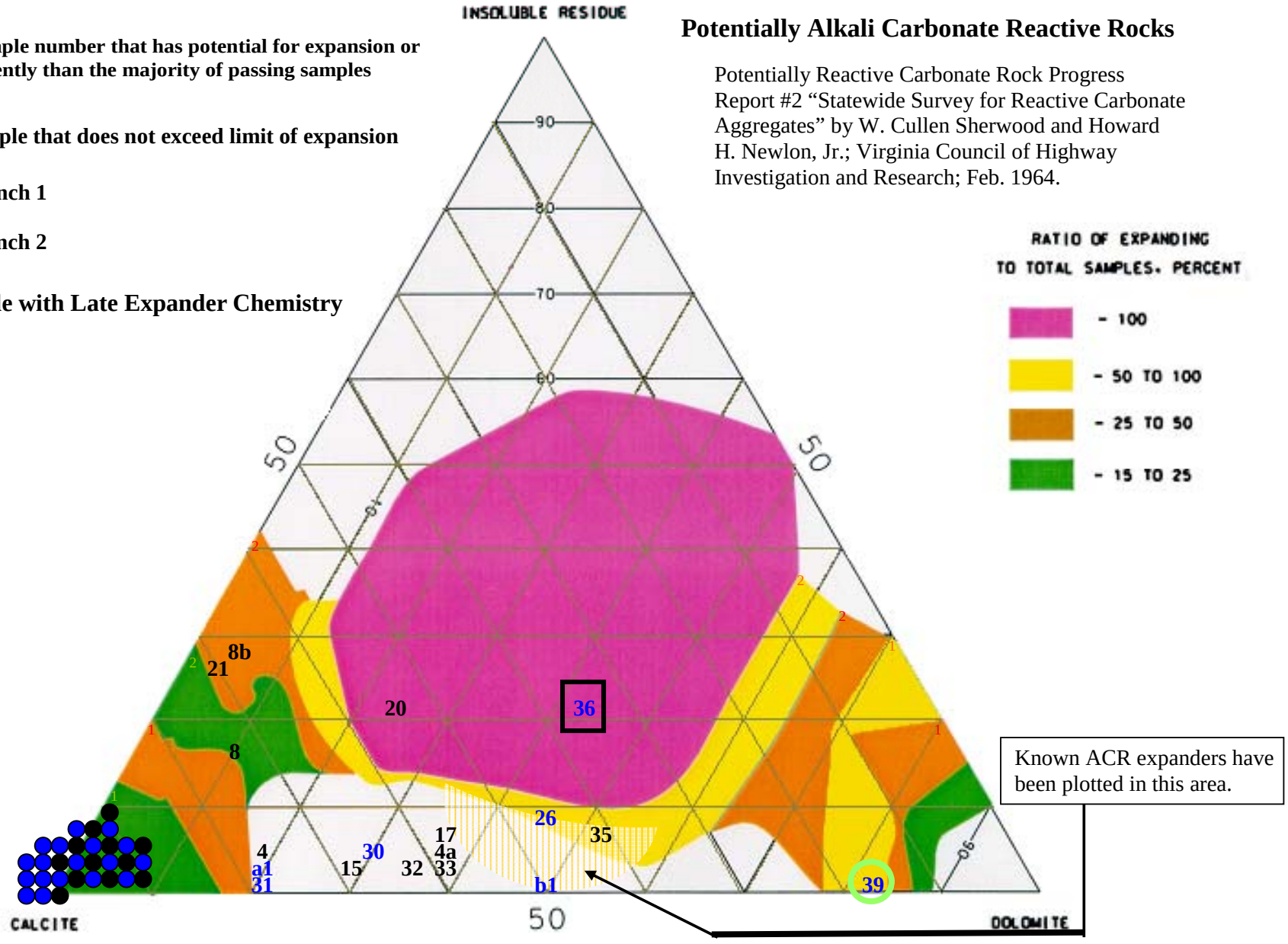
● or # - Bench 1

● or # - Bench 2

○ Sample with Late Expander Chemistry

Potentially Alkali Carbonate Reactive Rocks

Potentially Reactive Carbonate Rock Progress Report #2 "Statewide Survey for Reactive Carbonate Aggregates" by W. Cullen Sherwood and Howard H. Newlon, Jr.; Virginia Council of Highway Investigation and Research; Feb. 1964.



Dolomite Quarry

 # - core sample number that has potential for expansion or plots differently than the majority of passing samples

core sample that does not exceed limit of expansion

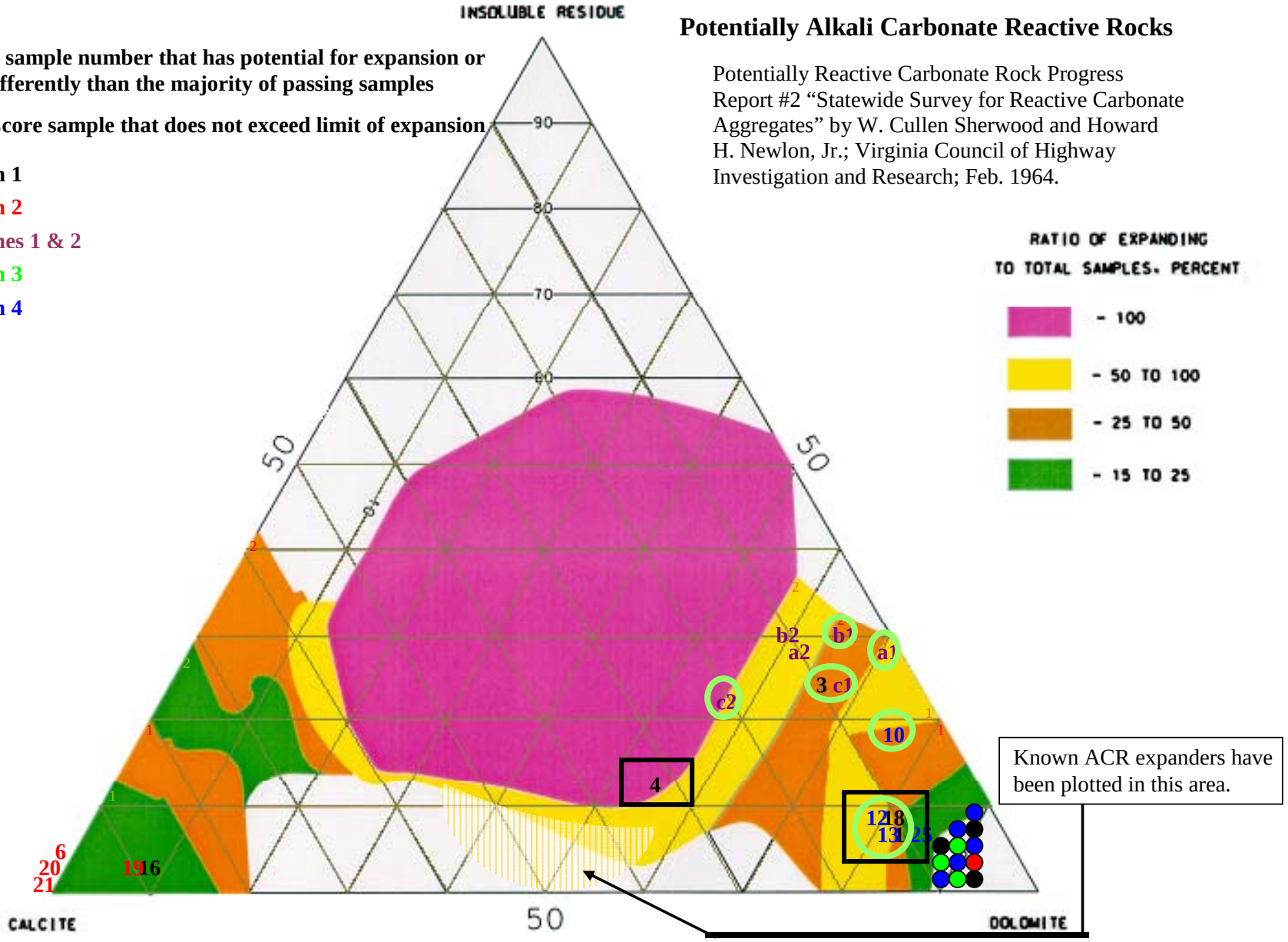
Bench 1

Bench 2

Benches 1 & 2

Bench 3

Bench 4



Potentially Alkali Carbonate Reactive Rocks

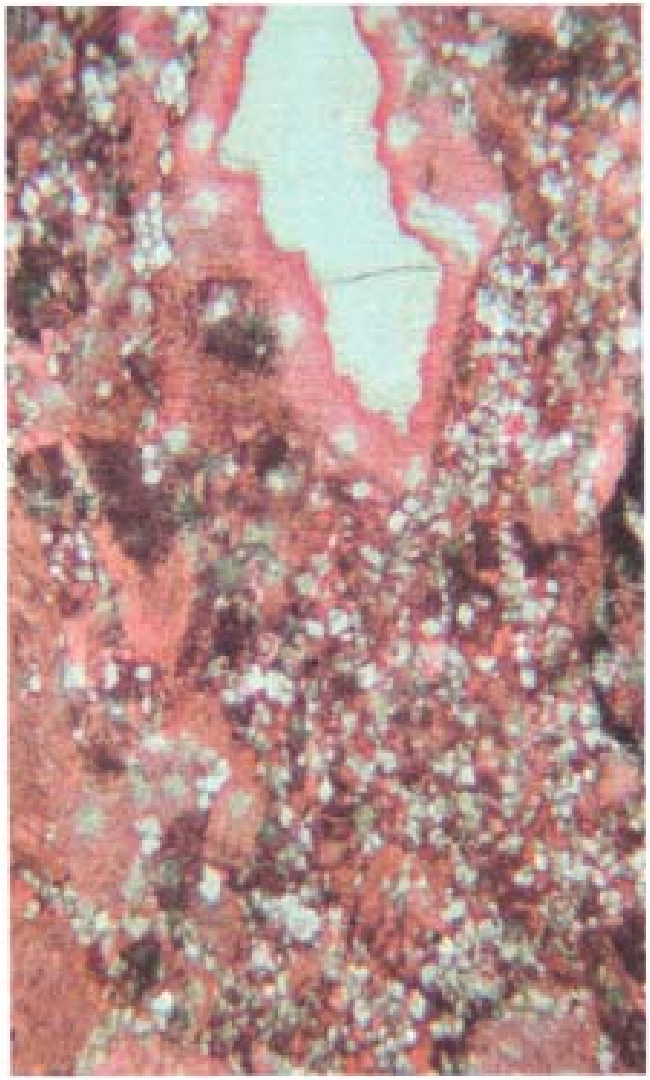
Potentially Reactive Carbonate Rock Progress Report #2 “Statewide Survey for Reactive Carbonate Aggregates” by W. Cullen Sherwood and Howard H. Newlon, Jr.; Virginia Council of Highway Investigation and Research; Feb. 1964.

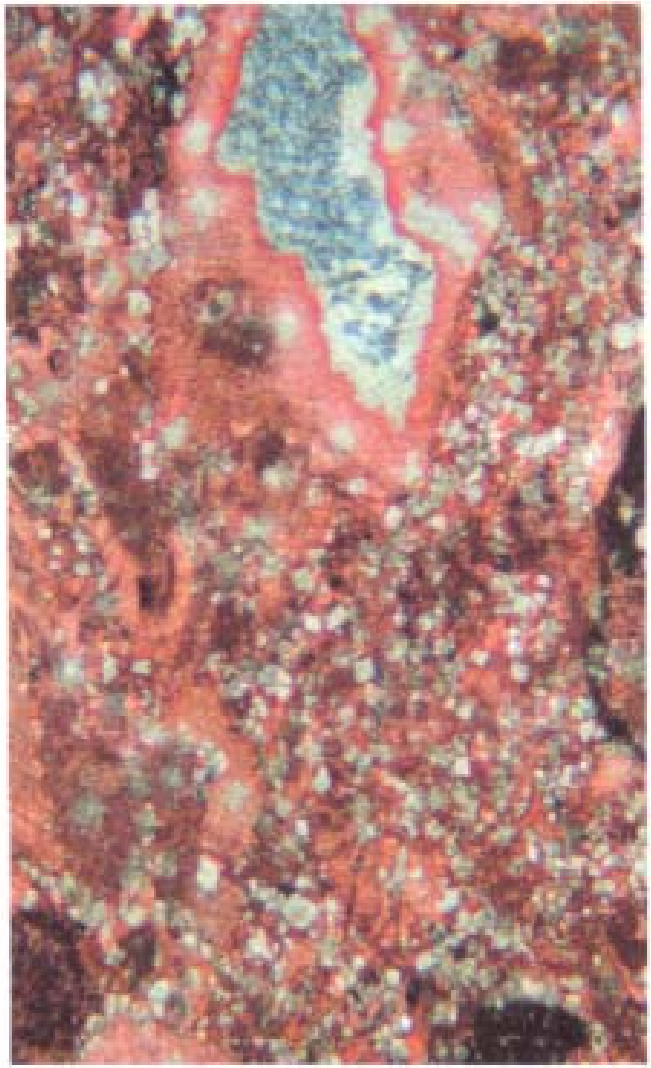
Petrographic Exam – Thin Sections

- When having the thin sections prepared, get half of the slide stained with red, this allows for very easy identification of the calcite and dolomite.
- Thin sections should be prepared for all samples in the questionable zones of the ACR Prediction Diagrams

Limestone Quarry #36
ACR & ASR Reactive Texture

PPL
25X





XN
25X

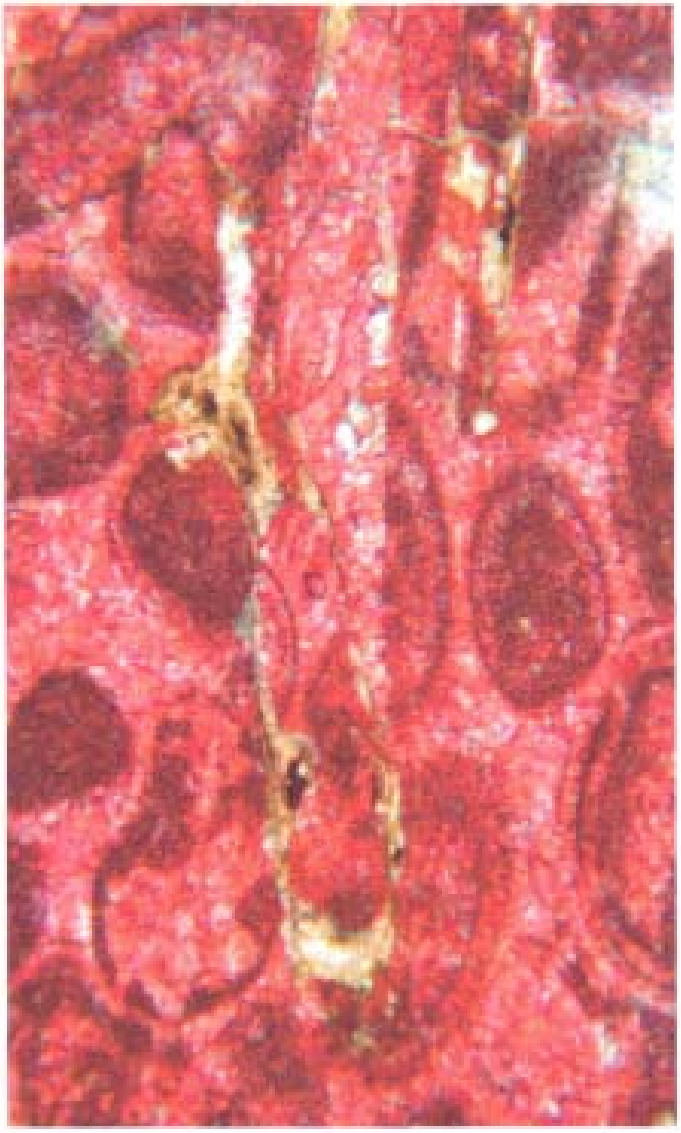
Limestone Quarry #10 &14 Less or Non-Reactive Textures

#10 63X PPL

Slight texture along a stylolite

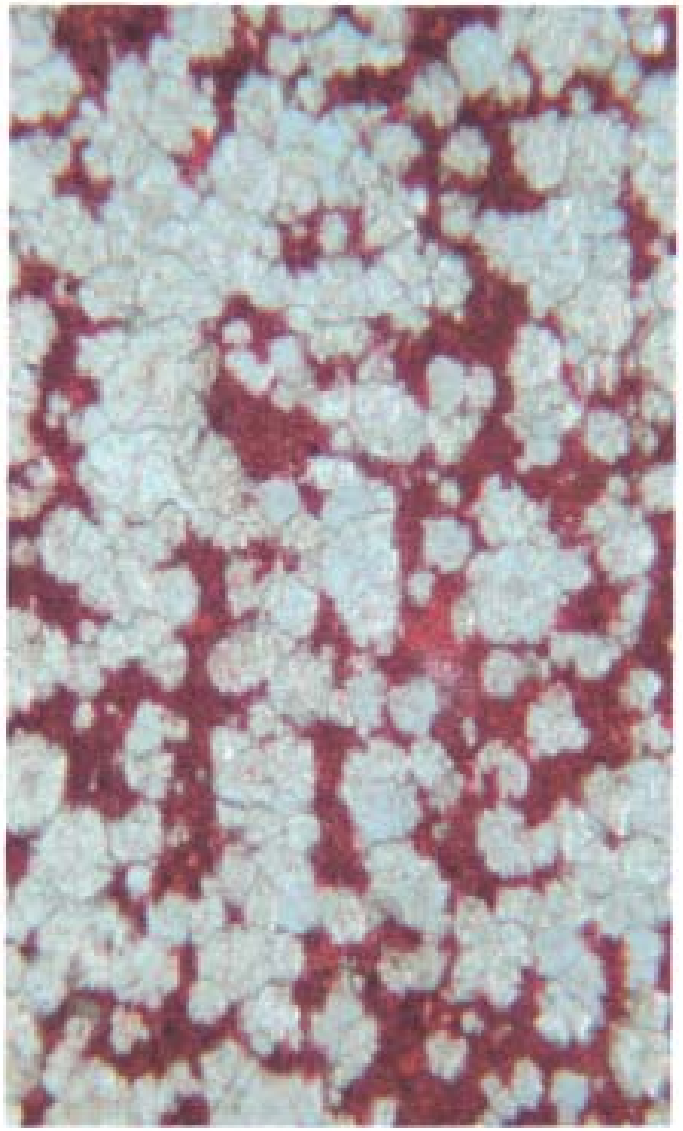
 # 14 63X PPL

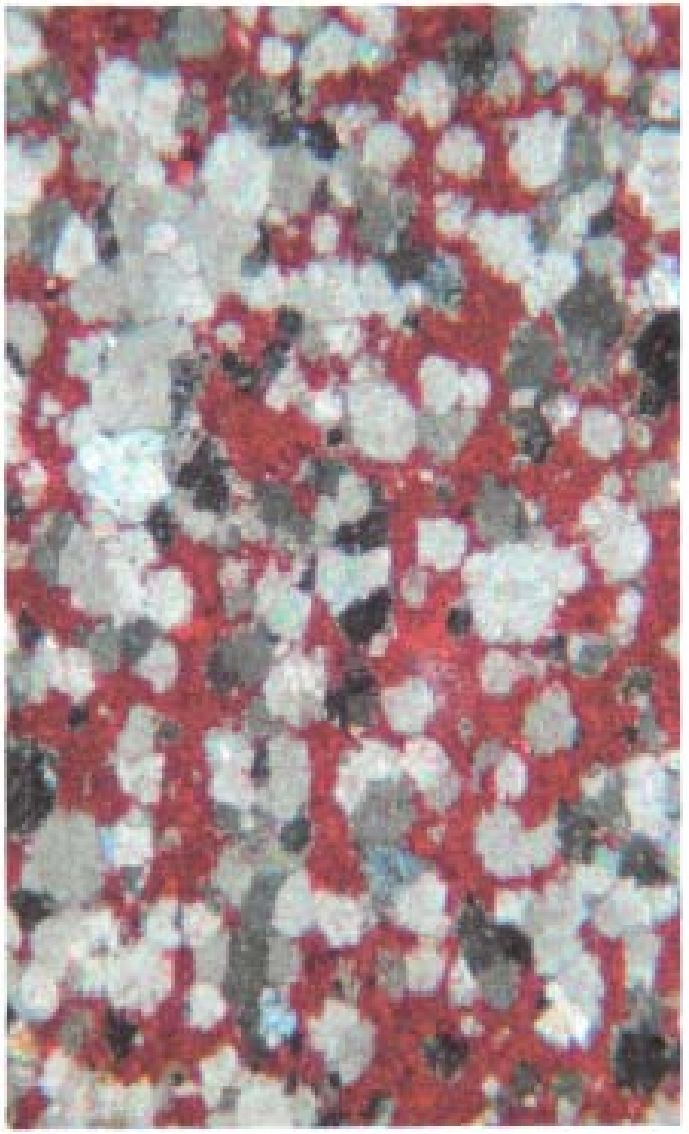
No ACR texture



Dolomite Quarry #4 Reactive Texture

PPL 63X





XN 63X

Dolomite Quarry #12&13 Non-reactive Textures

These had the chemistry of late expanders; from the texture, it is still possible but unlikely, the texture appears stable.

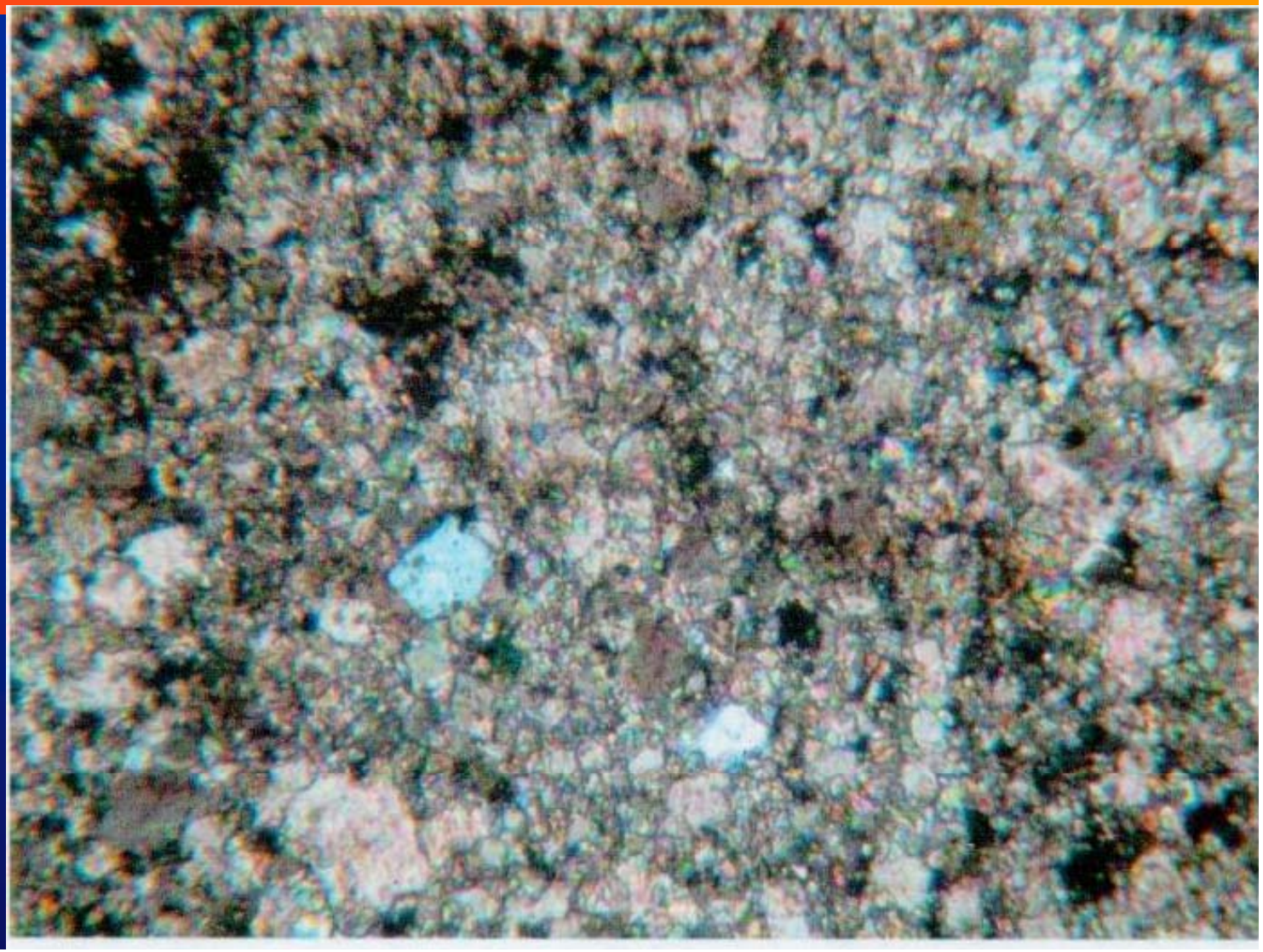
XN 63X

PPL 25X

Dolomite Quarry #18- Late Expander Texture

Ultra-thin Thin section, it has been stained, the slight pink tint is the calcite disseminated among the dolomite

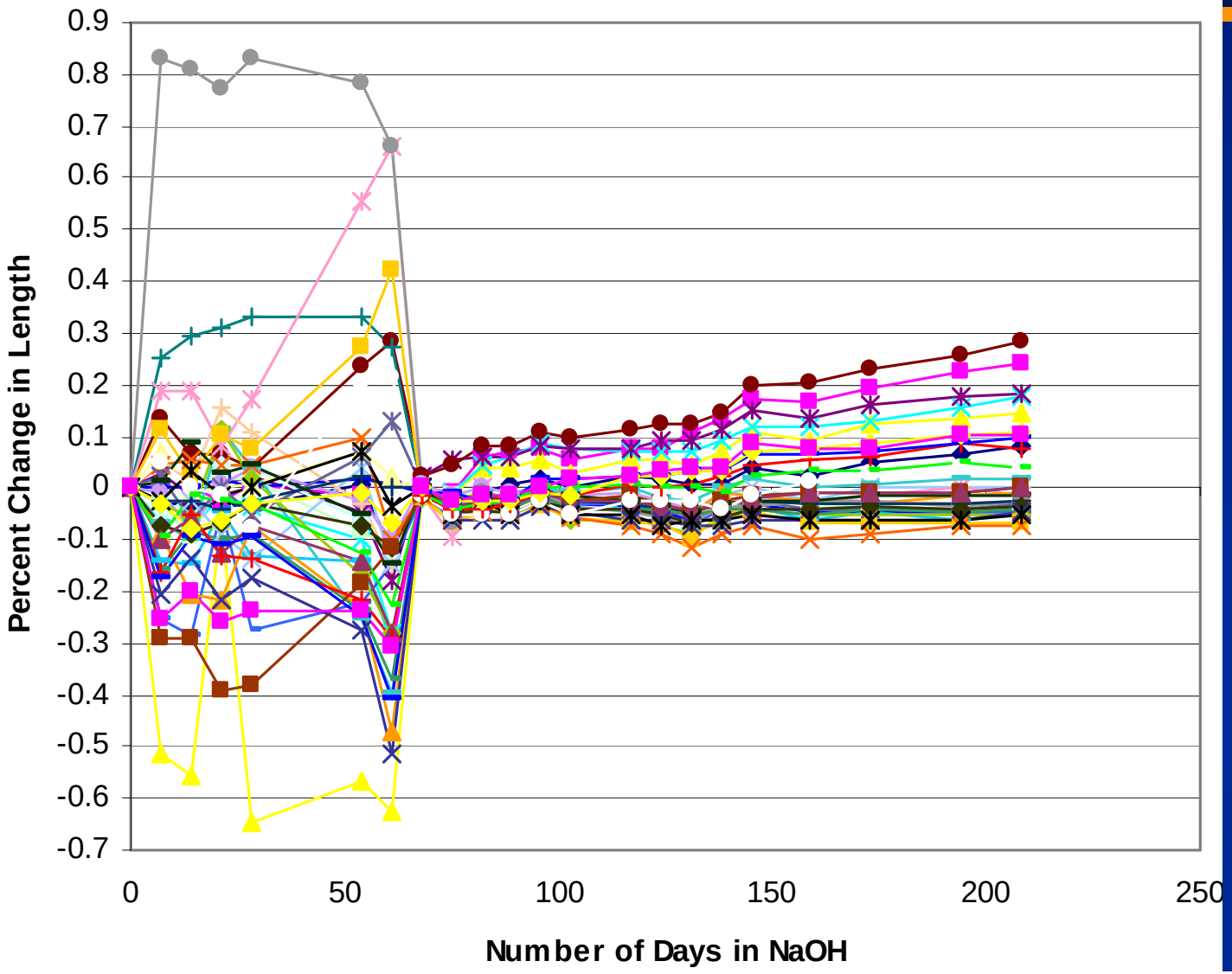
XN 63X



ASTM C 586 Rock Cylinder Method

- 586 samples should be chosen from the core after petrographic results (at least the x-ray) is completed. Corresponding expansion from a 586 with a reactive petrographic result will provide the best analysis of a quarry.
- Sampling from the ledge wall or the shotrock before the petrographics have been completed does not allow for good correlation between the tests. No matter how hard one attempts to match the shotrock/ledge rocks samples to the cores, it is never a sure match.

ASTM C 586 Sample Preparation



Ensure test cylinders have good smooth endpoints or the data will be erratic and wrong.

These samples had their point reground after 68 days in NaOH, early data was lost.

Aggregate Tests

- ASTM C 1105 Determination of Length Change of Concrete due to ACR – concrete mortar bar is stored in high humidity at 73º F for one year. Job concrete mix is used so the alkali content is what would be in the job.
- ASTM C 1293 Determination of Length Change of Concrete due to ASR – concrete mortar bar with high alkali cement is stored in high humidity at 100º F for one year. Extra alkali is added to force reaction. May be modified by decreasing alkali, adding supplemental cementitious materials, or using the job mix.
- Despite the titles ASTM C 1105 and ASTM C 1293 cannot distinguish between ACR and ASR if the mineralogy is present for both reactions.
- If both mineralogies are present, the theory is to run the test with sufficient cementitious materials to suppress the Alkali-Silica Reaction and thereby determine if the aggregate is also Alkali-Carbonate Reactive.

Preparations for ASTM C 1293/1105

- Because 1293 is run at 100ºF and 1105 is tested at 73ºF, 1293 is the harsher test; therefore running ASTM C 1293 should give a better estimate of the potential reactivity of an aggregate whether it is ASR or ACR.
- Federal Highway Administration recommends the modified ASTM C 1293 be run for 2 years; therefore, these tests need to be planned in advance.
- Criteria for the two year test is a combination of 1105 and 1293 - <0.015/3mon; <0.025/6mon; <0.03/1yr; <0.04/2yr.

ACR Mitigation for New Structures

- Avoid use of aggregate classified as potentially reactive by selective quarrying.
- Specify the use of low alkali cement and cementitious materials in the hope of keeping the alkali content of the concrete low enough the reaction will not start (< 2 kg/m^3).
- Dilute so the amount of potentially reactive rock is less than 20% of the coarse or fine aggregate or 15% of the total if reactive material is present in both.
- Specify the minimum aggregate size that is feasible for the project.

What to do if the aggregate is reactive.

- Hope it is a late expander and
- That you have already retired.

- The only thing that can be done then is slot cutting to release the expansion pressure in the concrete in the hopes of preventing cracking.

References

- ASTM STP 169B (1978), C (1994), and D (2006)
- Evaluation of the Potential for Expansion and Cracking of Concrete Caused by Alkali-Carbonate Reaction, C. A. Rogers, 1986
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- Use of the Accelerated Mortar Bar Test for Evaluating the Efficacy of Mineral Admixtures for Controlling Expansion due to Alkali-Silica Reaction, M. D. A. Thomas, F. A. Innis, 1999
- ACI Materials Journal 95-M71, Effect of Slag on Expansion Due to Alkali-Aggregate Reaction in Concrete, M. D. A. Thomas, F. A. Innis, 1998